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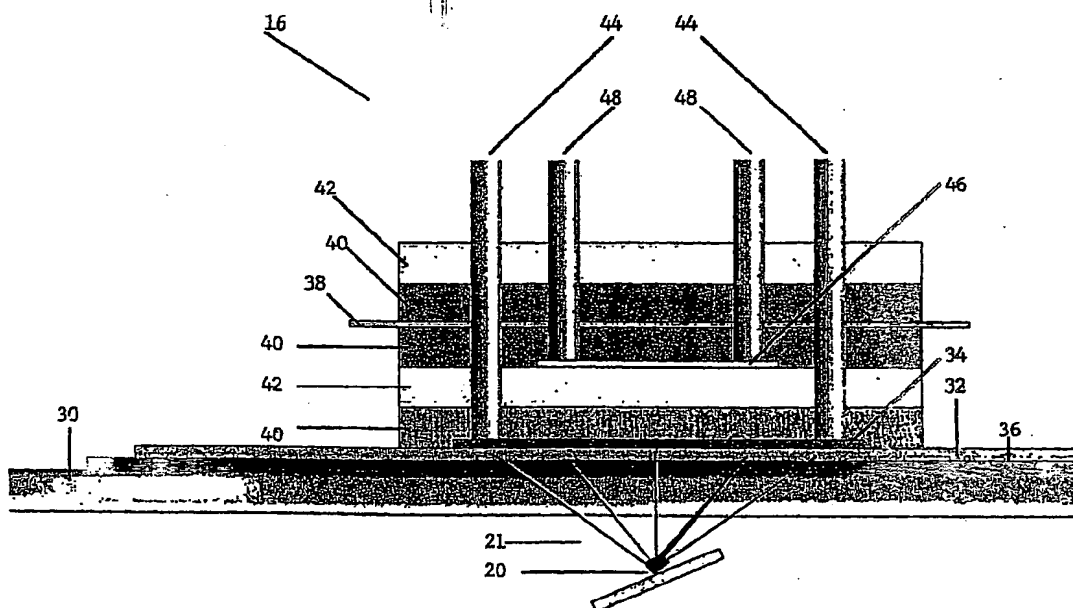
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(54) Title: PHOTOLYTIC OXYGENATOR WITH CARBON DIOXIDE AND/OR HYDROGEN SEPARATION AND FIXATION



(57) Abstract: Apparatus for oxygenating an enclosed space as well as removing carbon dioxide from the enclosed space. The apparatus comprises a photolytic cell (16) having an anode compartment with a photo-active surface having the ability to convert water to oxygen; a cathode compartment having the ability to convert carbon dioxide and hydrogen to a solid or liquid medium; and a light source (20) for providing light photons (21) to said photolytic cell and activating the photo-reactive surface.

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**PHOTOLYTIC OXYGENATOR WITH CARBON
DIOXIDE AND/OR HYDROGEN SEPARATION AND FIXATION**

This application claims priority to and extends the teachings and disclosures of the following applications: Provisional Application Serial No. 60/358,448 for Development of Photolytic Pulmonary Gas Exchange, Bruce Monzyk, et al., filed February 20, 2002; Provisional Application Serial No. 5 60/388,977 for Photolytic Artificial Lung, Bruce Monzyk et al., filed June 14, 2002; Provisional Application Serial No. 60/393,049 for Photolytic Oxygenator with Carbon Dioxide Fixation and Separation, Bruce Monzyk, et al., filed June 20, 2002; and PCT Application No. PCT/US02/24277 for Photolytic Oxygenator with Carbon Dioxide Fixation and Separation, Bruce Monzyk et al., 10 filed August 1, 2002; and Provisional Application Serial No. 60/404,978 for Photolytic Oxygenator with Carbon Dioxide and/or Hydrogen Separation and Fixation, Bruce Monzyk et al., filed August 21, 2002.

FIELD OF THE INVENTION

15

The present invention is directed to a photolytically driven electrochemical ("PDEC") oxygenator and carbon dioxide and/or hydrogen separator that uses light energy to achieve gas exchange in various media. The separated carbon dioxide and/or hydrogen is then removed or preferably reacted with and/or 20 captured by a substrate for subsequent removal and/or storage. The invention finds particular application in providing a proper physiological gas environment for humans, animals and microorganisms. It is also to be appreciated that the invention finds further particular applications in confined space areas such as the crew or cabin space of a submarine, space station, interplanetary vehicle, 25 extraterrestrial vehicle, subterranean mine, firefighting situations, chemical exposure, biological warfare, caves or tunnels, or other confined living areas.

BACKGROUND OF THE INVENTION

30

Oxygen depletion in confined spaces has always been a problem. Human beings need a constant supply of oxygen and the concomitant removal of carbon dioxide to live and function. When humans, microorganisms or other

animals are in confined spaces where the flow of gases from the atmosphere is impeded, the aforementioned supply of oxygen and the removal of carbon dioxide and/or hydrogen are critical to maintaining a proper physiological environment.

5 Known methods for providing oxygen generation and/or carbon dioxide removal include the electrolytic production of oxygen using KOH in water. While hydrogen and oxygen are produced, the simultaneous production of hydrogen results in problems concerning its safe capture, storage and disposal. This is particularly true in confined spaces such as in submarines where only a limited
10 supply of hydrogen gas can be safely stored. Additionally, venting of hydrogen gas into the outside ocean waters creates further difficulties concerning noise and detection issues.

An organic amine liquid carbon dioxide process has also been used to capture carbon dioxide which is complicated to operate and is sensitive to
15 motion. Moreover, on an emergency basis, lithium chlorate candles have been used to produce oxygen and lithium hydroxide powder to absorb carbon dioxide. These are hazardous materials and to be used under duress is very undesirable. These devices and processes for providing oxygen and removing carbon dioxide are briefly described below:

- 20
- Chlorate Candles – These are heated to cause the decomposition of the chlorate into oxygen gas and salt. In this operation the high heat required and sudden release of large amounts of pure oxygen gas are highly hazardous and limits the usefulness of this technology.
 - 25 • Potassium Hydroxide (KOH) Electrolysis – This technology is also hazardous as it emits explosive mixtures of O₂ and H₂ gases, and since KOH is strongly caustic and corrosive.
 - Lithium Hydroxide (LiOH) is used for CO₂ capture. However, this material is hazardous due to it being a caustic fine powder. It is spread
30 over the floor to generate a high surface area whereupon it leads to possible contact and/or ingestion by the crew causing illness and potential lung damage.

- CO₂ is also removed by large devices using liquid organic amines. These units are complicated processes and so are difficult to control. They also require large amounts of space, are heavy and sensitive to motion.

5 In addition, the first and third of the above listed technologies are "once use" technologies and so are spent after one use.

 Therefore, a need exists for new technology and approaches that have the potential to provide long term life support in confined environments. Such approaches and technologies shall include not only oxygen generation, but also
10 to the removal and/or capture of carbon dioxide and/or hydrogen.

SUMMARY OF THE INVENTION

 The enclosed invention uses photolytic energy to drive the production of
15 oxygen (O₂) gas and electrochemical fixation of carbon dioxide (CO₂) gas as a means to rejuvenate used, "stale" air, i.e. air low in oxygen and/or rich in carbon dioxide relative to atmospheric breathing air. The present invention produces breathable air for humans, animals, and aerobic or facultative aerobic microorganisms. In another embodiment, the present invention relates to the
20 fixation of hydrogen gas generated during the O₂ gas production into storable or useful products.

 More particularly, the present invention relates to a photolytically driven electrochemical (PDEC) oxygenation and carbon dioxide and/or hydrogen removal apparatus. The apparatus includes a photo-electro chemical cell
25 ("photolytic cell" or "photolytic module") that, in part, operates similar to the photosynthesis process that takes place in green plants. In the anode compartment, the apparatus utilizes the photolytic cell instead of electrical wiring to convert light energy in order to simultaneously generate oxygen and low voltage internal electrical energy. The photolytic cell also removes carbon
30 dioxide from the environment and converts it to a carbonate solid in the cathode compartment and/or fixed as an organic compound. One or more photolytic cells can be included in the apparatus of the present invention depending on the quantity, quality, etc. of desired gas exchange. These units can be collected in one area, or dispersed to provide multiple independent breathing air
35 maintenance units, including portable units.

In a further embodiment, the present invention relates to a process for collecting, venting, storing or converting hydrogen gas produced during the oxygen generation process. As mentioned above, the PDEC technology provides dissolved oxygen ("DO") production at the photo anode. The electrons (e-) and hydrogen ions (H⁺) released when dissolved oxygen (DO) is formed can be combined at the cathode to form hydrogen (H₂) gas. This H₂ can be collected and used to fuel a fuel cell, or can be safely vented to the atmosphere, e.g. via degassing tubing. However, in certain instances it is found desirable, and is a part of the herein described invention, that these e- and H⁺ ions can be used to further enhance the technology by using them to produce additional useful product(s). When these products are non-gaseous, then the technology can be used to avoid the generation of H₂(g), which is a safety and/or stealth issue in certain applications, for example in maintaining the breathing atmosphere in submarines.

The light energy utilized in the present invention is ultraviolet ("UV") light or visible light, with the laser form being the most preferred. However, the light energy can also be broad-band, received by the way of a "light pipe" fiber optic cable and/or by the way of an attenuated total reflectance (ATR) link.

In the apparatus of one preferred embodiment of the invention, dissolved oxygen (DO) is generated in the anode compartment from an aqueous solution by means of the light dependent chemical reactions, photolysis and disproportionation. This is followed by the removal or clearing of carbon dioxide in the cathode compartment by the formation of higher carbon compositions such as hexose sugar, carboxylic acids, aldehydes, alcohols, etc. Additionally, hydrogen can also be removed or cleared from the cathode compartment by reacting the hydrogen ions and electrons produced during the oxygen generation process with various substrates to produce additional useful products.

In this regard, photolysis is the initiation of a chemical reaction that results from the absorbance of one or more quanta of radiation. Here, water from an aqueous solution is converted into oxygen by a light-activated catalyst, such as a semiconducting metal oxide. The metal oxide is utilized as a photo-absorbent material or a photo-absorption element. It is photolytically irradiated to form, from water, hydrogen ions, hydrogen peroxide or other forms of oxygen gas

precursor (active oxygen, "AO") and electrons by the absorption of one or more quanta of electromagnetic radiation. The free electrons generated are then electrically conducted away to avoid reversal of the reaction and optionally utilized to drive various electrical devices, such as a pump. Additionally, the free
5 electrons can be utilized to fix or convert the carbon dioxide and/or hydrogen also generated by the process into other products.

For example, it has been found that active oxygen can be generated in a further embodiment of the present invention by the use of the anatase form of titania ($\text{TiO}_{2(a)}$) as the light absorbent material in the anode compartment. The
10 photo energy of light, such as ultraviolet laser light (about 350 nm), selectively excites TiO_2 semiconductor transition (about 350-390 nm band, or about 3.1 eV) with minimal material radiation or transmission. The ultraviolet energy produces charge separation in the anatase form of TiO_2 , which then produces active oxygen (AO) and free electrons. The free electrons are then subsequently
15 electrically conducted away due to the semi-conducting property of the anatase. Alternatively, other suitable light absorbent materials can also be utilized in the present invention at various wavelengths provided that the energy is sufficient to produce active oxygen.

Moreover, the active oxygen produced during photolysis can be
20 converted by means of manganese dioxide (MnO_2), or other disproportionation catalytic agents and/or processes, into dissolved oxygen (DO) and water.

Additionally, in the present invention, carbon dioxide can also be removed from the environment by the means of a series of carbon molecule building reactions. These reactions occur in the cathode compartment of the apparatus
25 to produce removable and/or recyclable carbonate solids.

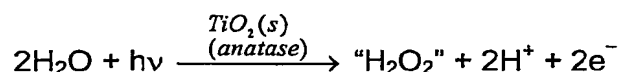
Similarly, hydrogen ions generated during the dissolved oxygen production can be reacted to produced, removable and/or recyclable hydrogen containing solids. In this regard, an electrochemically reducible compound is added to absorb the hydrogen ions and electrons to produce useful, or at least
30 easily disposable (environmentally neutral), compounds. The preferred compounds in this role are also safe enough to be used in confined environment, and have a large capacity for hydrogen ions.

Consequently, the apparatus of the present invention produces oxygen directly from an aqueous solution. At the same time, the apparatus also utilizes

the hydrogen ions and electrons produced from the aqueous solution to remove the carbon dioxide and/or hydrogen to produce a carbon or hydrogen containing solid or organic compound such as sugars, carboxylic acids, aldehydes or alcohols.

- 5 A brief description of the pertinent reactions involved in the embodiment of the present invention utilizing anatase, for example, as the light absorbent material (i.e. as the photolytic catalyst and MnO_2 as the disproportionation catalyst) is provided below:

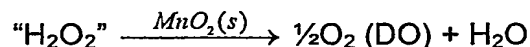
10 **Photolysis:**



where H_2O_2 is used to illustrate "active oxygen" intermediate.

15

Disproportionation:



- 20 DO = dissolved oxygen, which is readily converted to gaseous oxygen, $\text{O}_2(\text{g})$, for breathable air maintenance applications.

The above information shows the general chemical reactions involved in the anode compartment of the photolytic cell to produce dissolved oxygen.

25 Subsequent to this production, the electrons are conducted away, and the dissolved oxygen diffuses from the film surface to be collected and/or channeled to a confined environment.

- 30 Additionally, the hydrogen ions generated flow from the anode compartment to the cathode compartment. There they react with carbon dioxide and/or other compositions to form higher carbon materials, etc.

- 35 In a further aspect, the present invention is also directed to a photolytic cell. The photolytic cell includes a transparent substrate or window. An anode (such as a metal film) is adjacent to the transparent window. A photolytic coating containing a light-activated catalyst and a disproportionation catalyst abuts the anode. An anolyte cell flow through area is adjacent to the light activated catalyst. An optional cation exchange membrane borders the anolyte cell flow through area. A catholyte cell flow area abuts the cation exchange

membrane. A cathode is present adjacent to the catholyte and is connected to the anode.

In an additional aspect, the present invention is further directed to a method for delivering oxygen to an enclosed or restricted environment. The method comprises moving an aqueous solution, such as an electrolyte solution, into a photolytic cell wherein light is utilized by a light-activated catalyst to produce oxygen from water and moving the oxygen generated out of the photolytic cell into the enclosed environment. The free hydrogen ions generated by this process can be optionally utilized to convert carbon dioxide or other substrates to carbonate compositions and/or additional useful products.

In a further aspect, the present invention relates to the direct photolytic conversion of water to liquid phase oxygen (dissolved oxygen), with commensurate clearance of carbon dioxide and hydrogen. A test flow cell is provided comprising a conductive coating of vacuum-deposited titanium (Ti) metal, adherent TiO_2 (anatase), and MnO_2 , applied as a laminant to a glass substrate. Long wavelength (low energy) UV laser light, directed to the transparent glass substrate, reproducibly resulted in the generation of H_2O_2 , an active form of oxygen (active oxygen), which was subsequently converted, by the catalytic action of MnO_2 , to dissolved oxygen. Oxygen gas is then extracted from the dissolved oxygen through an oxygen gas separator and collected or channeled to a closed or constricted living environment. Additionally, carbon dioxide present in the closed or constricted living environment is removed by reacting the carbon dioxide with other carbon sources and catalysts to form carbonate solids. The hydrogen form during the oxygenation process can also be utilized to produce easily disposable and useful compounds. Based on these results and others, the photolytic cell or module may be used, employing multiple parallel photolytic surfaces to improve O_2 yield and CO_2 and hydrogen clearance.

These and other objects and features of the invention will be apparent from the descriptions set forth below.

BRIEF DESCRIPTION OF THE DRAWINGS

The present invention will become more fully understood from the detailed description given below, the claims and the accompanying drawings.

5 The description and drawings are given by the way of illustration only, and thus do not limit the present invention.

Figure 1 shows a schematic view of an embodiment of the photolytic cell that can be utilized in the present invention.

Figure 2 is a schematic of a generalized embodiment of the invention
10 wherein an alpha-keto pentose source is used to remove carbon dioxide.

Figure 3 is a schematic of another embodiment of the invention wherein carbon dioxide and a pentose are used to prepare a C₃ carbon based intermediary for carbon dioxide removal.

Figure 4 is a schematic of another embodiment of the invention showing
15 details of a rubisco-catalyzed reaction used to prepare a C₃ carbon intermediary for carbon dioxide removal.

Figure 5 is a schematic of a more detailed embodiment of the invention showing the rubisco catalyzed reaction and the chemical steps in greater detail.

Figure 6 is a schematic of another embodiment of the invention wherein
20 the carbon dioxide is reacted with the pentose directly in the PDEC cell.

Figure 7 is a graphic illustration demonstrating the use of a PDEC apparatus for providing oxygen in a confined environment.

Figure 8 is a graphic illustration showing the use of the PDEC apparatus
25 for producing oxygen and removing carbon dioxide in a confined environment to produce a carbonate solid.

Figure 9 is a graphic illustration demonstrating oxygen production and carbon dioxide removal by the production of C₆ compositions from two C₃ intermediaries or a C₅ compound and carbon dioxide.

Figures 10A and 10B are illustrations of the geometries of two
30 microfabrication structures of the present invention.

Figures 11A - 11C are illustrations of examples of potential nanopatterned surfaces utilized in the devices of the present invention.

Figure 12 is an illustration of a potential 3-D mesh structure utilized in the devices of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

Oxygen is essential to the respiration of animal life. The function of respiration is to provide the energy needed by body cells. Cells obtain this energy mainly by metabolizing glucose with oxygen, so they require a constant supply of oxygen. In addition, the waste products of the metabolic process – mainly carbon dioxide – must be carried away from the cells.

Respiration includes the breathing of air into the lungs, the transfer of oxygen from the air to the blood, the transport of oxygen in the blood to the body cells, the metabolisms of glucose with oxygen in the cells, and the transport of carbon dioxide to the lungs to be breathed out.

The present invention is directed to the process of providing oxygen and removing carbon dioxide from confined space areas. More particularly, the present invention is directed to a photolytically driven electrochemical (PDEC) oxygenator and carbon dioxide and/or hydrogen removal apparatus. The apparatus may be used for controlling the environment in a closed or restricted volume in order to make the volume habitable to humans, animals and aerobic microorganisms. The apparatus achieves a gas balance typical for that required by the humans, animals or aerobic microorganisms in at least part of the enclosed volume or confined living space.

The photolytically driven electrochemical (PDEC) oxygenator and carbon dioxide and hydrogen removal apparatus includes a photo-electrochemical cell (or photolytic cell) that in part operates similar to the photosynthesis process that takes place in green plants. The photolytic oxygenator apparatus utilizes the photolytic energy to drive oxygen generation from water. The oxygen is then released to the confined volume. The photolytic cell also converts carbon dioxide to a higher carbon compound, such as a C₆ sugar-type compound, that can be stored as a solid, gel or liquid, which then fixes the CO₂ thereby removing it from the confined space. This higher carbon compound can optionally be recycled in the form of a food or energy source. Other fixed CO₂ organic and inorganic compounds can be formed as well.

Additionally, the present invention is directed to the removal of hydrogen which accumulates during the oxygen generation process in the PDEC apparatus. As described previously, the PDEC technology provides dissolved

oxygen (DO) production at the photo anode. The electrons (e-) and hydrogen ions (H⁺) released when DO is formed can be combined at the cathode to form H₂ (gas). This H₂ can be collected and used to fuel a fuel cell, or safely vented to the atmosphere. Moreover, in certain instances it is found desirable that these e- and H⁺ ions can be used to further enhance the technology by using them to produce additional useful product(s). For example, an electrochemically reducible compound can be added to absorb the hydrogen ions and electrons to produce useful, or at least easily disposable compounds. The preferred compounds are not only safe enough to be used in confined environments, they also have a large capacity for hydrogen ions and electrons.

In the PDEC apparatus of the present invention, oxygen is produced in the anode side of the PDEC apparatus. The oxygen produced at the anode side of the photolytic oxygenator apparatus is typically produced in an aqueous electrolyte solution such as a brine, seawater, etc. The oxygenated liquid so formed then flows out of the photolytic oxygenator apparatus. It is degassed and the oxygen gas is sent back to the closed or restricted volume area for breathing by humans, animals or aerobic microorganisms.

The carbon dioxide is removed by the cathode side of the PDEC apparatus of the present invention. Gas containing carbon dioxide from the enclosed volume is reacted with an aqueous liquid at pH > 4, and preferably > 6, to extract carbon dioxide into the liquid so that it can be fixed by formation of organic acids or organic acid salts, for example, glycerate or sugar acid, etc., which is transported and treated in the cathode portion (or cathode compartment) of the photolytic cell to form a solid or syrup, for example a sugar-like compound.

The hydrogen is also removed from the cathode side of the PDEC apparatus. As discussed more particularly below, the hydrogen is reacted with various substrates, including various carbon compounds referenced above, in order to fix the hydrogen into easily removable and useful compounds.

In an additional embodiment, the present invention is directed to the use of a photolytic cell as a novel respiratory assist device and process. The apparatus of the invention includes one or more photolytic cells having photochemically active material and associated components for the production of oxygen, the removal of carbon dioxide and hydrogen, and the co-production

of electrical power. The electrical power can be used to produce additional chemical changes or reactions. Optionally, the invention may include a photolytic chamber to house or hold a sufficient number of stacked or assembled photolytic cells to perform the rate of gas exchange desired.

5 In a further embodiment of the present invention, a semi-conducting metal oxide is used as the photo-absorption element. This semi-conducting metal oxide is the anatase form of titania, or TiO_2 . Photolysis of this oxide results in the generation of active oxygen, in a manner, which is considerably more long lasting than photosynthetic pigments (i.e. the chlorophiles).
10 Importantly, the light energy associated with activation by a 354 nm UV laser light selectively excites the TiO_2 semiconductor electronic transition (350-389 nm band, or about 3.2 eV) with minimal wasted radiation or transmission. Special dopants and/or other metal oxides, such as WO_3 and ZnO , can be used to adjust this wavelength, in order to reduce the energy requirement and even to
15 allow activation within the range of visible light. UV energy produces charge separation in the anatase, which then produces active oxygen, hydrogen ions and free electrons, the latter being electrically conducted away. Diffusion layers are minimized through the use of electron conductance to and from the photolytic site by photolytic transparency over a large surface area and by
20 electrochemical conduction.

The active oxygen is then converted to dissolved oxygen through the use of a disproportionation catalyst such as MnO_2 . Importantly, this apparatus has the ability to efficiently generate both fluid phase oxygen (i.e. dissolved oxygen) and gas phase oxygen (i.e. PO_2).

25 Taken from a broad perspective, this embodiment of the present invention includes the following system components: 1) an aqueous phase, 2) photolytic energy to provide "charge separation" in a thin film, 3) electrical energy, produced from the electrons of the "charge separation" photolytic reaction, 4) chemical reactions driven by the photochemistry, i.e. H_2 and DO
30 generation, 5) the removal of CO_2 through the generation of carbonate solids or fixed CO_2 organic compounds, and 6) the removal of hydrogen ions and electrons through the hydrogenation production of useful and/or easily disposable compounds.

The invention can also use mesoporous, amorphous, microporous, nanophased, crystalline, heterogeneous, or homogenous materials and coatings, and the like, alone or in combination to provide high-surface area active coatings to photolytically drive chemical changes, photochemical changes, electricity generation, and/or electrochemical changes in fluid streams, preferably adjacent to the coating/material, or, in the case of electricity, electrical current driven into wires attached to the coating directly, or via a electrical conducting intermediate material. The said fluid can be liquid or gas or sol gel or conducting solid or porous solid.

Figure 1 shows one of the flow-through embodiments of the photolytic cell 16 of the present invention. In this flow-through cell embodiment, the following main components of the photolytic cell 16 are assembled, i.e. a conductive coating of vacuum deposited Ti metal 36, a coating of adherent TiO₂ (anatase) 32, an optional MnO₂ particulate layer 34. A UV laser light 20 was shown on the transparent glass or quartz substrate 30 so to initiate the reactions.

In this regard, the photolytic cell 16 of Figure 1 includes a transparent window 30 or wave guide for the entry of light energy in the form of photons 21 from a light source 20 such as an ultraviolet laser light. On one side of the glass slide is an anode conductor layer 36, such as titanium (Ti) metal film. Attached to the anode conductor layer 36, is a layer of a light activated catalyst 32 such as anatase (TiO₂). An optional catalyst layer 34, such as manganese dioxide, is adjacent to the light activated catalyst layer 32. The photolytic cell 16 includes one or more layers of silicone gaskets or spacers 40 and an acrylic housing 42. A pair of anolytes 44 (in/out) is connected to the light activated catalyst layer 32 or optional catalyst layer 34 and extend through the photolytic cell 16 away from the transparent window 30. The photolytic cell 16 further includes a cation exchange member 46, such as a NAFION[®] membrane from DuPont. A pair of catholytes 48 (in/out) is connected to the cation exchange member 46 and extends outwardly through the photolytic cell 16 generally away from the transparent window 30. The photolytic cell 16 further includes a cathode layer 38, such as Pt foil, adjacent to the cation exchange member 46. The operation and use of this embodiment of the invention is more particularly described below.

Figure 2 is a schematic drawing showing the electrical and chemical transformations which occur in the PDEC cell 16 of the apparatus 10. Electrolyte or anolyte 128, such as NaCl brine, NaSO₄, K₂SO₄, HCl, and the like enters the anode compartment 100/44 of the photolytic cell 16 through inlet 12 by way of an optional peristaltic pump 14. Light photons (hv) 21/114 generated by light source 20 enter through a transparent window 30 or waveguide and activate the light activated catalyst 32 present in photo-reactive surface 116 such as 100 μm TiO₂ (anatase). The light activated catalyst 32 either directly converts water in the electrolyte 128 to dissolved oxygen or converts water to active oxygen and hydrogen ions and an optional second catalyst 34, such as manganese dioxide (MnO₂) on a porous film, converts active oxygen (e.g. H₂O₂) into dissolved oxygen (DO). The oxygen then exits the anode compartment 100/44 by the way of outlet 13 and is pumped by an optional pump 132 to oxygen gas separator 118. At the gas separator 118, the gaseous oxygen is provided to a confined air space 120 for usage.

The electrons released from the conversion of water from the electrolyte to oxygen are collected in the collector electron anode 110. An electrical current formed from a battery or other source (not shown) allows the electrons to flow from the anode 110 to the cathode 108, such as graphite or nickel, so that the electrons do not react with the active oxygen to cause a back reaction and the reformation of water.

The electrical current and electron flow can be regulated by a current regulator or resistor (not shown). The hydrogen ions formed from the conversion of water at the light activated catalyst diffuse from the anode compartment 100/44 across the optional membrane 126 to the cathode compartment 102/48.

In the cathode compartment 102/48, stale air 104, which is rich in CO₂ relative to atmospheric breathing air, is contacted with i) a liquid such as brine containing α - keto pentose containing a catalyst typically of mixtures of Mg²⁺/PO₄³⁻ electrolyte to convert carbon dioxide into dissolved form in the liquid; and ii) C₃ pentose obtained from stores 122 which also contains a catalyst to form glycerate or the equivalent. The glycerate is electrochemically reduced at the surface of the cathode and reacts with the hydrogen ions which previously

immigrated from the anode compartment 100 to the cathode compartment 102 to form a hexose (C_6) sugar. The hexose sugar solution then flows out of the cathode compartment 102 into separator 112. In separator 112, the liquid is separated and then recycled 134 and the hexose sugar is placed in C_6 stores 114 or utilized as an energy source for the crew, etc.

The various particular components and/or processes of the flow through PDEC cell embodiment of the present invention are described in more detail below:

1. Transparent Substrate or Window 30

The transparent window 30 can be formed from glass, quartz slides, quartz, etc. Glass is useful in forming the transparent window provided that the UV transparency is adequate at the wavelength needed. Quartz slides are also useful because of its high UV transparency. For the transparent window, light entry into and through the transparent window can be from the back, side, or bottom. Edge illumination through the transparent window can optionally include a lens or wave guide.

The transparent window can further include a wave guide. A wave guide uniformly distributes photons ($h\nu$) from the light over the surface of the light activated catalyst. Particularly, the wave guide causes the light photons to travel in a path so that the photons maximally contact the entire layer of the light activated catalyst. Light enters the wave guide in the side of the transparent window generally parallel to the surface of the light activated catalyst that is attached to the transparent window. The wave guide allows for maximal light photon contact with the light activated catalyst without directly illuminating the side of the entire light activated catalyst attached to the transparent window. The wave guide also allows for maximal photolytic cell staking because light is not required to directly illuminate the light activated catalyst but rather can be indirectly illuminated by side or edge entry in the transparent window. The wave guide provides additional efficiency to light used in the photolytic cell because the light can be spread across the entire surface of the light activated catalyst.

2. Anode Conductor Layer 110

The anode conductor layer 110 conducts electrons formed from the reaction of water to oxygen out of the anode. The anode conductor layer prevents the electrons from reacting back with the oxygen to reform water, thereby allowing maximal formation of oxygen. The anode conductor layer is applied or attached to at least one side of the transparent window 30.

The anode conductor layer 110 can be formed at least two different ways. The anode layer can be formed by attaching a thin film of uniform metallic conductor to the transparent window using vapor deposition. The film preferably has a thickness of less than about 0.2 μm . Preferably, the film is formed from gold or titanium. Gold remains metallic at all conditions but can be very efficient at UV light blockage or reflection. Titanium can be oxidized to TiO_2 by adding O_2 to the deposition chamber to yield a possible catalyst layer with excellent adhesion.

The anode conductor layer 110 can also be formed by using photo-resist technology. Under photo-resist technology, grids are prepared with masks using vapor deposition. Conductor line spacing, width and thickness optimization may be required to prevent excessive attenuation, and provide sufficiently close conductive areas to sweep electrons away from the light activated catalyst layer.

3. Catalysts 32 and 34

A light activated catalyst 32 is coated onto the anode conductor layer. The light activated catalyst is photochemically activated and reacts with water to form dissolved oxygen or a free radical oxygen intermediate that is ultimately converted to dissolved oxygen. The term active oxygen (AO) in the present application defines any free radical oxygen intermediate formed in the photolytically catalyzed reaction of water that is ultimately converted to dissolved oxygen. The active oxygen formed is in the form of a peroxide, such as hydrogen peroxide, H_2O_2 , or peroxide ion salt, hydroxyl free radical, super oxide ion, etc., and is converted into dissolved oxygen in the presence of a catalyst. The active oxygen formed depends on the light activated catalyst used. Also, depending on the light activated catalyst used, water may be photolytically converted directly into dissolved oxygen without first forming an active oxygen.

Several different catalysts can be employed for producing dissolved oxygen photochemically. One catalyst that can be used to photochemically produce oxygen is zinc oxide. By using zinc oxide, peroxide (H_2O_2) is produced directly from water. H_2O_2 is an excellent form of active oxygen for providing
5 sufficient potential diffusion distance, and also for the disproportionate reaction to dissolved oxygen and water via a solid MnO_2 catalyst (similar to green plant O_2 generation site) occurring photochemically at < 340 nm by way of metal ion assisted disproportionation with catalase and other hydroperoxidases. Zinc oxide film has other positive attributes including, known film formation
10 technology (e.g. via the zinc/nitrate/glycine reaction), low toxicity concerns, and low cost.

An additional catalyst that can be used to photochemically produce dissolved oxygen is tungstate (WO_3) that is exposed to visible light and using e^-_{scb} removal. WO_3 yields oxygen (O_2) directly from water without the need to first
15 produce an active oxygen species. Oxygen is generated stoichiometrically and the "back reaction" is unfavored so that there is not significant competition to the direct formation of dissolved oxygen. Only visible light is needed to generate dissolved oxygen from WO_3 , no more than about 496 nm. WO_3 films present low toxicity concerns. Preferably, the use of WO_3 further includes the removal of
20 excess e^-_{scb} formed during oxygen formation from water.

Another catalyst suitable for reacting with water is TiO_2 (anatase) irradiation with, followed by dissolved oxygen production at a metal catalyst, such as a MnO_2 catalyst, or other similar catalyst. TiO_2 removes the e^-_{scb} efficiently from the production area in order to ultimately obtain good dissolved
25 oxygen production and minimize any back reaction to reform reactants. The removal of e^-_{scb} is performed through conduction via the semi-conductor property of the $\text{TiO}_{2(a)}$ with enhancement via application of a small DC bias voltage. TiO_2 irradiation also presents low toxicity concerns. TiO_2 provides very high insolubility and kinetic inertness to minimize dissolution and fouling during
30 use and maintenance. Preferably, UV light is chopped or pulsed during TiO_2 irradiation to allow time for the chemical reactions to occur since with continuous irradiation causes the e^-_{scb} to accumulate and force a back reaction to form water. A pause in the irradiation allows time for the slower, but still extremely fast irradiation in the range of @sec to msec to occur to occur.

A further catalyst for reacting with water to ultimately form dissolved oxygen is a semiconductor powder (SCP)-filled UV/VIS light transparent thermoplastic film. SCP-filled thermoplastic film is relatively inexpensive to manufacture and form into shape. SCP film is easily moldable, extrudable, cut
 5 and machined. SCP can be used very efficiently in surface applied only form. Also, SCP has low toxicity concerns. Optimized commercial products (conductive plastic filler powders) are available with good properties for dispersion, particle-to-particle electrical conductivity (for e^-_{sch} removal), and resistance to sloughing off that can be used with the present apparatus.

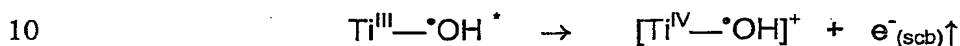
10 The following additional preferred conditions may be used for each of the above-mentioned catalysts. First, an application of a small (e.g. up to a few volts DC) bias voltage can be applied to help ensure that the e^-_{sch} is quickly conducted away from the production site. Second, a chopped illumination, instead of a continuously applied illumination, may allow secondary chemical
 15 reactions to occur since the secondary chemical reactions are slower than the photochemical reactions and enhance photo yields by allowing the excited electrons to exit the system and not be present for regeneration of starting material, i.e., water.

Of the above-mentioned catalysts, the TiO_2 (anatase) catalyst followed by
 20 a second metal catalyst for disproportionation is the most preferred. When the TiO_2 catalyst is used, the light-titania interaction is the first step in the ultimate formation of dissolved oxygen. It is known that surface hydrated particulate TiO_2 (anatase) solid, $TiO_{2(a)}-OH_2$ or $Ti^{IV}O_{2(a)}-OH$, is an efficient UV light ($h\nu$) acceptor at wave lengths <390 nm, resulting in active oxygen formation from
 25 sorbed water and hydroxyl groups. The most probable reaction is believed to be:



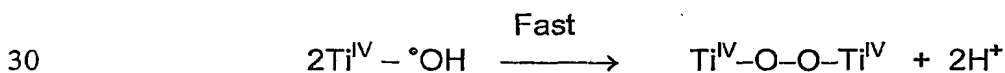
It is noted that other bonds to Ti have been omitted for clarity. The
 30 reactant and product of the above reaction are solid materials. In the above reaction, H_2O is already bonded to the surface of the $TiO_{2(a)}$ catalyst as H_2O or as hydroxyl ion (OH^-), i.e. $Ti^{IV}O_{2(a)}-OH_2$ or $Ti^{IV}O_{2(a)}-OH$, respectfully. Hence, no atoms are required to move during the very fast photon absorption process.

The * represents a low lying excited electronic state where the energy of the photon is used to transition or excite an electron from a nonbonding orbital on the oxygen to a molecular orbital centered on the titanium ion, hence converting the titanium into a trivalent oxidation state. The molecular orbital centered on the titanium ion is known to be a part of the semiconduction band ("scb"), and so the electron is readily conducted away from the site to form a bipolar charged grain, or, if connected to a closed DC electrical circuit, resulting in full charge separation, i.e.,

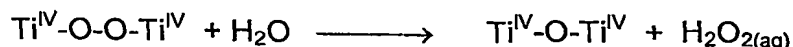


If the e_{scb}^- is not conducted away or otherwise removed by reaction with an oxidant present in the solution, the e_{scb}^- could react with the hydroxyl free radical and reverse or back react so that the system would return to its original state and form water. In this latter case there would be no net reaction and the photolytic energy will appear as a small amount of heat. Hence the charge separation process and removal of e_{scb}^- is considered an important first step of the photolytic cell dissolved oxygen generation process.

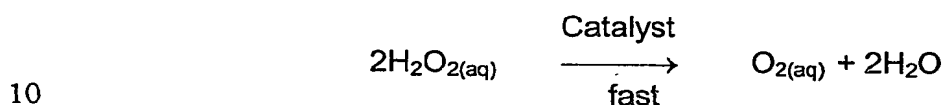
The hydroxyl free radical (OH^\bullet) group present is used to represent the initial form of the active oxygen generated by the photolytic process. It is not certain that OH^\bullet is the dominant species present when $\text{TiO}_{2(a)}$ is photolyzed. The active oxygen formed could generally be in the form of a superoxide, hydrogen peroxide, or a hydroxyl free radical. However, the form of this active oxygen produced has sufficient thermodynamic driving force to form active oxygen from water. For the $\text{TiO}_{2(a)}$ catalyst at neutral pH, these highly reactive hydroxyl free radicals either back react as described above, or rapidly dimerize to form (μ -peroxo) titanium (IV) and hydrogen ions, i.e.



Another way to increase the amount of dissolved oxygen production in the $\text{TiO}_{2(a)}$ system is to provide a means to speed the rate of release of the trapped μ -peroxide as hydrogen peroxide as to active oxygen.



H₂O₂ is an excellent form for the active oxygen species as it readily
 5 migrates and is easily catalyzed to disproportionate into dissolved oxygen and
 water.



Therefore, for the TiO_{2(a)} photocatalyst to be useful, a means for releasing
 the μ-peroxide energy is needed, such as soluble H₂O₂, since H₂O₂ can diffuse
 15 to the MnO₂ for dissolved oxygen production, or by conducting the oxidizing
 power to another active oxygen form, such as SFRs in the adjacent solution that
 can be used in dissolved oxygen production, or using the Ti^{IV}-O-O-Ti^{IV} content to
 electronically remove electrons from the MnO₂ cluster/particle (as is done in
 green plant photosynthesis by the "D" protein). In the last means, only an
 20 electron flows from the water through the MnO₂ to the μ-peroxo linkage through
 delocalized bonds. This electron replaces the e⁻ lost from the TiO_{2(a)}-OH system
 as e⁻_{sch}.

The formation of H₂O₂ as the active oxygen is valuable since H₂O₂ can be
 rapidly converted to dissolved oxygen in 100 % yield using many different
 25 methods: thermally; metal ion catalysis; particulate/surface catalysis; base
 catalysis; and free radical reaction with reductant initiation. Preferably, metal ion
 catalysis, such as, MnO_{2(s)}, provides an efficient catalyst for H₂O₂
 disproportionation to water and O₂, on thin film substrate constructs.

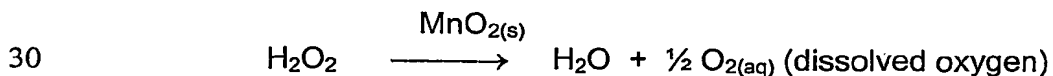
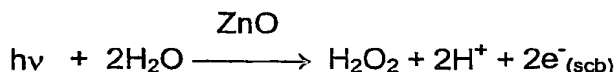


Photo catalyst systems such as zinc oxide, ZnO, release peroxide as the
 active oxygen more readily than does TiO₂. Less acidic metal ions under the
 Lewis acid/base theory definition cannot sufficiently stabilize the highly alkaline
 35 peroxide ion relative to water protonation (pK_{a1} of H₂O₂ is 11.38 (25°C)) to form

it within the solid phase, and so hydrogen peroxide, H_2O_2 , is readily formed from ZnO:



5

ZnO films and particles can be prepared in a number of ways with varying but controlled composition, morphology and porosity. For example, mirrors of zinc, doped zinc, and zinc alloys and can be sputtered down onto an optically transparent support, followed by oxidation with $\text{O}_{2(\text{g})}$. This treatment produces a metal/metal oxide (Zn/ZnO) film. Another highly effective approach to semiconducting ZnO-based films is to utilize a process for optical glass coatings. (L.R. Pederson, L.A. Chick, and G.J. Exarhos, U.S. Patent 4,880,772 (1989).) The optical glass coating technique is based on applying a zinc nitrate/glycine aqueous solution as a dip or spray, followed by drying (110°C for 15 min), then heating ($450\text{--}500^\circ\text{C}$ for 3 min) to initiate a self-oxidation reaction during which the carbon and nitrogen exits as gases leaving an adherent yet porous film bonded to the underlying surface (e.g. glass) and is referred to as the glycine nitrate process. (L.R. Pederson, L.A. Chick, and G.J. Exarhos, U.S. Patent 4,880,772 (1989).) The ZnO film is normally produced doped with alumina by including aluminum nitrate in the aqueous formulation for the initial dip. Many other metal ion blends are also possible with this technique.

Tungstate only requires visible light to produce dissolved oxygen, and produces dissolved oxygen directly without requiring a second catalyst to form dissolved oxygen. The lower photon energy requirement for WO_3 is due to the smaller band gap of 2.5eV versus at least 3 eV for $\text{TiO}_{2(\text{a})}$. As with the TiO_2 anatase system, high yields are possible with the WO_3 catalyst if the e^-_{scb} is removed. The production of O_2 increases very significantly if RuO_2 (ruthenium oxide) is placed on the surface of the WO_3 . This is consistent with the fact that RuO_2 is a known good catalyst for O_2 production and so represents a route to improving other approaches.

An advantage may exist if the dissolved oxygen producing film could be a filled plastic. Such materials are often inexpensive and manufactured easily. Commercial sources exist for semi-conducting, low light absorbing, inorganic fillers for plastics which are supplied in ready made condition for incorporation

into plastics, making the plastics electrically conductive. For example, E.I. duPont Nemours, Inc. sells electroconductive powders (EPC) under the trade name ZELEC® ECP for such purposes. The conductive substance in ZELEC® ECP is antimony-doped tin oxide ($\text{SnO}_2\text{:Sb}$). The bulk of these materials, onto which the conductor is coated, are familiar inorganics such as mica flakes, TiO_2 , and hollow silica shells, or ECP-M, ECP-T and ECP-S respectively. Pure $\text{SnO}_2\text{:Sb}$ -based material is designated ECP-XC and is a much smaller particle than the other materials. About 25-45% by weight of the ECP products are used so that the particles are sufficiently close to each other to provide internal electrical connections throughout the otherwise non-conducting plastic. ECP-S and ECP-M normally perform best for lower concentrations. Thin films of ECP-XC can provide an attractive coating because they are very fine grained and strongly light absorbing.

The TiO_2 layer can be formed a variety of ways. The TiO_2 layer can be formed by sol gel, drying and baking. A product under the trademark LIQUICOAT® from Merck & Co., Inc., which hydrolyzes Ti(OR)_4 type material in water to form TiO_2 and 4ROH can be used to form the TiO_2 layer under a sol gel/drying/baking process. TiO_2 can also be formed from preparing an anatase suspension from dry powder, then dipping, drying, and baking the suspension to form the TiO_2 layer. Another way the TiO_2 layer can be formed is by e-beam evaporating titanium and subsequently exposing the titanium to O_2 within a deposition chamber. The TiO_2 layer can also be formed by adding titanium salt to water and adjusting the pH to $\sim 2-7$ to form a suspension, then dipping the suspension and allowing the suspension to dry.

Active oxygen is created from TiO_2 by irradiation with UV light, but the chemical form of the active oxygen is very reactive and can be lost by side reaction occurring in close proximity to the TiO_2 particle surface where active oxygen is generated. There are at least three ways to minimize the loss of active oxygen to unwanted side reaction: 1) move the active oxygen to dissolved oxygen conversion point closer to the active oxygen generation point, i.e. move the metal ion catalyst as close as possible to the TiO_2 , which may require intimate contact between these two materials, in the order of angstroms; 2) electrically connect the two points, as is done in photosynthesis by a protein capable of conducting electrons; or 3) convert the active oxygen into a longer

lived intermediate active oxygen species that has time to migrate to more distant MnO_2 centers for conversion to dissolved oxygen.

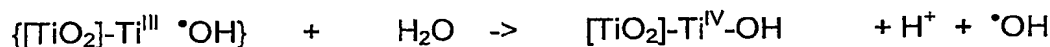
The amount of active oxygen lost by side reactions can be minimized by introducing an active oxygen carrier molecule into the media, or "D," by analogy to a photosynthetic system. Agents for use with species D can be selected from two groups, those that readily form organic peroxides, and those that form "stable" (i.e. long-lived) free radicals. Organic peroxides are useful because they easily produce dissolved oxygen when contacting MnO_2 , and readily form by oxygen insertion. The organic peroxide reactions are as follows:

10



where the excited electronic state corresponds to the ligand-to-metal charge transfer (free radical pair), and is followed by the reaction:

15



where conduction of the e^- into the semiconductor conduction band and away from the side of the particle near the $\cdot\text{OH}$ prevents recombination of that e^- . As shown in the reaction above, the TiO_2 anatase is regenerated. The above reaction produces a hydrogen ion for eventual CO_2 removal. Also, the active oxygen produced in the above reaction is in close proximity to TiO_2 as a free radical hydroxyl groups, $\cdot\text{OH}$.

As $\cdot\text{OH}$ is extremely reactive, lasts only for a very short time and does not diffuse far. One way to increase the amount of time that $\cdot\text{OH}$ is present is by introducing a species that stabilizes the $\cdot\text{OH}$. Similar to photosynthesis, a species "D" is introduced into the test system to capture the hydroxyl free radical in a longer lived species. The species D is generally shown the in following chemical reaction:

30

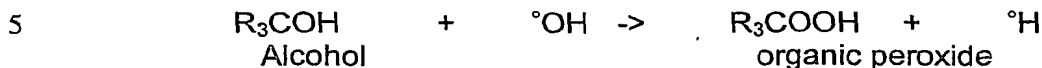


where D can be RC(O)OH :



organic peracid

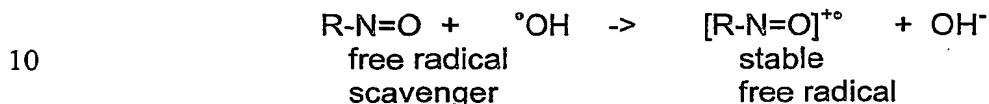
or D can be R_3COH :



Alcohol

organic peroxide

or D can be a free radical scavenger that forms a stable free radical:



free radical
scavenger

stable
free radical

or D can be 2,6-di-tertbutyl phenol:



The 2,6-di-tertbutyl phenol is the most desired D species, as a strongly reducing $\cdot\text{H}$ radical is not formed that would consume OH^- and $[\text{TiO}_2]\text{-Ti}^{\text{III}}$ in wasteful reactions, regenerate the starting materials, and result in a low photochemical yield.

The catalyst used to convert active oxygen into dissolved oxygen includes metal ions capable of redox cycling, such as Fe^{II} , Fe^{III} , Cu^{I} , Cu^{II} , Co^{II} , Co^{III} , Mn^{II} , Mn^{III} , Mn^{IV} , etc., or metal oxides formed from metal ions capable of redox cycling, such as manganese dioxide, MnO_2 . The present reaction produces dissolved oxygen directly from water and by-passes the gaseous state. The MnO_2 catalyst is most preferred because it forms dissolved oxygen efficiently and is not highly selective of the active oxygen form.

One way to facilitate the conversion of active oxygen to O_2 is by doping the surface of the TiO_2 anatase with manganese (Mn). Surface doping the TiO_2 with Mn provides a highly productive active oxygen to O_2 conversion catalyst. Active oxygen disproportionation is rapid when dropped on a Mn-doped anatase. Alternatively, active oxygen can also be converted to O_2 by placing MnO_2 on the surface of the anatase in conductive form. In this form, electrons are catalytically passed from water to the active oxygen region of the anatase. Such an arrangement more closely mimics photosynthesis O_2 production.

Another way to convert active oxygen to O₂ in the photolytic cell is by using a MnO₂ octahedral molecular sieve (MOMS) material as the dissolved oxygen catalyst. The MOMS material has an open gel-like structure and is closely related to zeolites in structure. The MOMS material is easily formed from manganese salts through precipitation and drying.

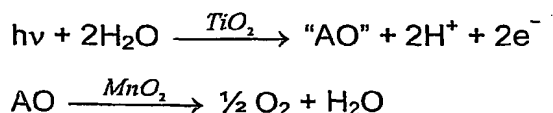
Active oxygen may also be converted to O₂ in the photolytic cell by a superoxide dismutase (SOD) catalyst. SOD catalyst is already available in the human body and can provide the required conversion of active oxygen, e.g. as O₂⁻, into a dissolved oxygen precursor, i.e. H₂O₂, to supplement the photolytic cell and Mn-doped anatase.

Alternatively, quinone can be replaced with Fe(CN)₆³⁻. The quinone or Fe(CN)₆³⁻ Q could be in homogeneous solution or film form.

4. Membrane 126

The cation exchange membrane 126 allows for the diffusion of cations in the photolytic cell. Particularly, the cation exchange membrane allows a cation, such as a hydrogen ion (H⁺) from water to diffuse through the membrane and subsequently react in the catholyte. The cation exchange membrane is commercially available under the trademark NAFION[®] and is available from E.I. du Pont Nemoirs Inc. NAFION[®] cation exchange membranes are a perfluorosulfonic acid/PTFE copolymer in an acidic form. Although NAFION[®] cation exchange membranes are the preferred membrane, one skilled in the art would recognize that other cation exchange membranes are also suitable in the photolytic cell.

The anodic compartment of the photolytic cell has the following series of reactions:



The two electrons formed in the anodic reaction are conducted away to the cathode via the anode conductor layer. The two H^+ ions are moved to a catholyte via a cation exchange membrane.

In a further embodiment of the invention, where optionally used, the cation exchange membrane allows for the diffusion of cations in the photolytic oxygenator apparatus. Particularly, the cation exchange membrane allows a cation such as Na^+ , K^+ , H^+ , Mg^{2+} , Li^+ , NH_4^+ , NR_4^+ , $CR=CH_3--$ produced during the oxygen making step to diffuse through the membrane and subsequently form a C_6 compound from either two C_3 compounds or from a C_5 compound and CO_2 .

5. Catholyte 108

The two hydrogen ions react with the electrochemically reduced glycerate in the cathode compartment 102 to produce hexose sugar (C_6) and like compositions.

6. Light Supply 20

The light supply is used in the photolytic cell to provide the photon energy necessary to activate the catalyst converting water into oxygen. The light source can be from any known light source including, but not limited to, sunlight, UV light, laser light, incandescent light, etc., depending on the activation requirement for the light activated catalyst used.

The light source may provide a particular wavelength of light depending upon the catalyst used. When tungstate (WO_3) is used as a light activated catalyst, the light source exposes visible light in order to activate WO_3 . When TiO_2 or ZnO is used as a light activated catalyst, the light source used has a wavelength in the UV range.

Preferably, the light source used in the cell is a laser light. The wavelength of laser light can be manipulated in order to attain a higher efficiency in exciting the light activated catalyst and forming active oxygen. Also, laser light allows the photolytic artificial lung to dissipate less overall heat. The laser light can be directed in a small area to energize the light activated catalyst and avoid contact or irradiation with other components of the cell. A particularly preferred laser light that can be used to activate TiO_2 is an argon laser at 364

nm (400 mwatts/cm²), which has a total power of about 2 watts, although other UV sources, including an HG arc lamp at 365 nm line, are also available.

It is preferred that the light from the light source be evenly spread within the photolytic cell. The even spreading of the light from the light source allows
5 for maximal excitation of the catalyst in order to convert more water into either active oxygen or dissolved oxygen. Along these lines, light from the light source can enter the photolytic cell through the transparent window from many positions. Light from the light source can enter directly through the transparent window and come into contact with the catalyst. Alternatively, light can enter the
10 transparent window from a side, back, bottom, or corner position and move through the transparent window by a wave guide to provide photon energy and excite the light activated catalyst. Side entry of light into the transparent window of the photolytic cell occurs at about at least a 68° angle. Preferably, side entry of light into the transparent window occurs at an angle of from about 70° to
15 about 80°.

7. Sensors Monitoring Reaction Chemistry

The apparatus can include one or more sensors that monitor the different chemical reactions occurring within the photolytic cell. The sensors can be used
20 to measure for potential toxins and toxin levels. Various sensors and sensor systems can be used including visual observations of color changes of redox indicator dyes or gas bubble formation, closed electrical current measurements and pH measurements, and dissolved oxygen probe analysis. Gas chromatography assays can also be performed. A dissolved oxygen probe can
25 be used to test and monitor O₂ generation, as dissolved oxygen, in real time. Also, the cell can incorporate one or more portals to insert a dissolved oxygen probe, CO₂ probe, pH monitor, etc. in different locations if necessary. The cell can also incorporate separate sampling chambers to trap gas bubbles for testing. These sampling chambers could also incorporate a device, such as a
30 septum for a hypodermic needle for instance, to obtain a sample for further testing. One skilled in the art would recognize numerous sensors could be used for monitoring the reaction chemistries occurring within the photolytic cell.

The photolytic cell can also include one or more process regulator devices that respond to the readings provided by the sensors. The process

regulator devices increase or decrease the amount of dissolved oxygen or CO₂ output, lower toxin levels, etc., depending on the requirements of the environment or of the photolytic cell.

Laminar flow is minimized within the apparatus. Minimization of laminar flow is accomplished by using current commercial cells, such as electro dialysis, electrodeionization, etc. Commercially available cells accommodate electrodes, membranes, and thin liquid chambers with flow distributors, and provide good seals and corrosion resistance. The cells are available in lab scale units for process development work. A particularly preferred commercial cell is the FM01-LC device from ICI Chemicals and Polymers, Electrochemical Technology, Cheshire, UK.

8. Power Source

The power source may be a nuclear reactor, electrical generator, hydroelectric energy, solar energy, battery pack, fuel cell and the like that is capable of providing energy for light production. As mentioned above, light may be from a laser, solar or other device capable of providing light at the appropriate wavelengths for the PDEC cell.

20 Modifications of the PDEC Apparatus to Avoid Hydrogen Gas Generation

As described previously, the PDEC technology provides for dissolved oxygen (DO) production at the photoanode. The electrons (e⁻) and hydrogen ions (H⁺) released when dissolved oxygen is formed can be combined at the cathode to form hydrogen (H₂) gas. This hydrogen gas can be collected and used to fuel a fuel cell, or safely vented to the atmosphere, e.g. via degassing tubing, etc.

Additionally, in certain instances it is found desirable, and is a part of the herein described invention, that these e⁻ and H⁺ ions can be used to further enhance the technology by using them to produce additional useful product(s). As discussed in more detail below, these additional products include organic and inorganic carbon based products and others. When these products are non-gaseous, then the technology can be used to avoid the generation of H₂(g), which is a safety and/or stealth issue in certain applications, for example in

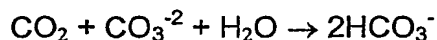
maintaining the breathing atmosphere in submarines. Below follows a description and examples of such useful non-H₂(g) products including those also provided by carbon dioxide sorption/fixation, provided by the invention.

5 A. Carbon Dioxide [CO₂(g)] Sorption/Fixation

As CO₂ is released by animals during breathing, this gas accumulates within the blood and the breathing air. It is critical to remove this CO₂ from blood to prevent acidification of the blood (acidosis), a potentially fatal situation. It is also critical to control CO₂ levels in confined-space breathing air for the same reason. Examples of such confined spaces include submarines (military and research), the space shuttle, the space station, mining activities, fire fighting, gas warfare, germ warfare, scuba diving, and the like.

In the current invention, CO₂ is absorbed using alkalinity or by photoelectro-chemical reduction. For example,

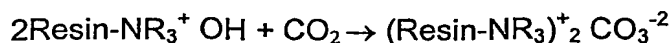
- 15 1. The fixation by 5-carbon sugars to make 6-carbon sugars (already described above)
2. Sorption by hydroxide ions (examples include alkali and alkaline earth metal hydroxides, such as LiOH, NaOH, KOH, RbOH, CsOH, Mg(OH)₂, Sr(OH)₂, Ba(OH)₂. Other examples include quarternary ammonium hydroxides, such as (CH₃)₄N⁺ OH⁻, R₄N⁺ OH⁻ (where R=alkyl, aliphatic
- 20 hydroxides, such as (CH₃)₄N⁺ OH⁻, R₄N⁺ OH⁻ (where R=alkyl, aliphatic alcohol, aromatic, and mixtures thereof).
3. Reaction with carbonates (e.g. sodium carbonate, potassium carbonate, quarternary ammonium carbonates), where the CO₂ sorption reaction is,



- 25 Where the CO₃⁻² can be presented as an aqueous solution and/or as an anion loaded onto an anion exchange resin. Such resins and solution can initially contain hydroxide ion (number two above). For example, where resin = anion exchange resin such as quarternary ammonium functionalized crosslinked polystyrene or quarternary ammonium functionalized crosslinked
- 30 methylmethacrylate gels, e.g.,

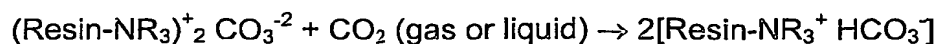


or



followed by,

5



The above carbonates are then reduced to non-gaseous compounds, such as formate ion, methanol, etc., electrochemically at an electrode using the electrons from the photolytic anode and the H^+ ions from the anode, or from added acid or buffer.

B. PDEC-based Hydrogenation Production of Useful Products

Once ribulose-type formation model compounds fix CO_2 as carboxylic acid, or as carbonate/bicarbonate ions form in the PDEC device (see above), such compounds internally produced, or added separately, can be used to generate useful compounds and/or prevent the need to form H_2 gas using the H^+ and e^- produced at the photo anode, i.e.



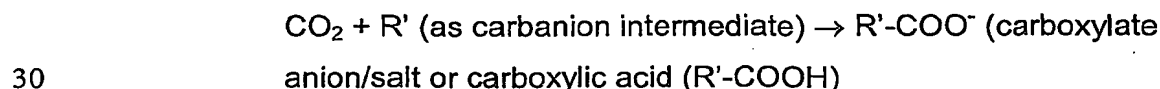
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Such H_2 Formation Alternative Examples of the invention follows:

1. The carboxylic acid is reduced to aldehydes and alcohols using the H^+ ions and electrons produced from the photo-anode of the PDEC cell. For example:

25

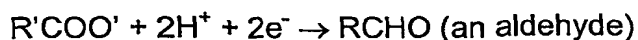
CO_2 Fixation into an Organic Compound:



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where $\text{R}'\text{-COO}^-$ represents fixed CO_2 .

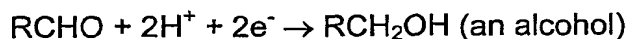
Followed by,



- 5 This reaction consumes the hydrogen ions and electrons produced by the photolysis reaction, thereby avoiding the production of H_2 (g).

To absorb even more H^+ and e^- , the above reaction is preferably also followed by,

10



Numerous suitable electrochemical reductions involving 2H^+ and 2e^- can be found in the following references:

- 1) "Electrochemistry", Vol. 5, The Chemical Society (publ.), Burlington
15 House, London, England, 1975, Sr. Reporter H.R. Thirsk.
2) Kirk-Othmer Encyclopedia of Chemical Technology,
"Electrochemical Processing (Organic)", Vol. 9, (1994), and
references contained therein.

- 20 2. An electrochemically reducible compound is added to sorb the H^+ ions and electrons to produce useful, or at least easily disposable (environmentally neutral), compounds. The preferred compounds in this role are also safe enough to be used in confined environments, and have a large capacity for H^+ ions and electrons. They may even be edible to provide
25 nourishment for the crew in the confined space. For example:

- a. Trioxane [i.e. cyclic and polymeric $(\text{CH}_2\text{O})_3$, especially 1,3,5-trioxane (CAS No. 110-88-3)]
b. Trioxane derivatives [i.e. cyclic and polymeric [cyclic $(\text{R}_1\text{R}_2\text{C}-\text{O})_3$, where
30 $\text{R}=\text{a sugar moiety (especially edible), alkyl, aryl, combinations thereof, etc.}$]
c. Formaldehyde, and aqueous solutions thereof
d. Paraformaldehyde, and aqueous solutions thereof.

e. Non-toxic and/or edible aldehydes, especially glucose, xylose, maltose.

e.g. $\text{d-glucose} + 2\text{H}^+ + 2\text{e}^-(\text{cathode}) \rightarrow \text{d-sorbitol}$

e.g. $\text{d-mannose} + 2\text{H}^+ + 2\text{e}^-(\text{cathode}) \rightarrow \text{d-sorbitol}$

Reference: Chemical and Metallurgical Engineering, No 10, October
1937, p 588 by R.L. Taylor.

f. Electrochemical reduction of carbonates, for example at a zinc cathode,
i.e.

$\text{CO}_3^{2-} + 2\text{H}^+ + 2\text{e}^-(\text{cathode}) \rightarrow \text{HCOOH}$ (yield ~ 100%)

Reference: "Organic Electrode Processes", by Milton J. Allen (Reinhold
Publ. Co., New York, NY), 1958, p 70, including references 45 and 46
contained therein. This reference is also a source of many other possible
electrochemical reduction candidates that avoids releasing substantial
amounts of H_2 gas from the PDEC cell. For example, the reduction of
benzaldehyde to benzyl alcohol: $\phi\text{CHO} + 2\text{H}^+ + 2\text{e}^-(\text{cathode}) \rightarrow \phi\text{CH}_2\text{OH}$
(p 71).

C. Carbon Dioxide Fixation by Electrochemical Capture Using Anionic Intermediates:

Examples of compounds that may be used, among others, to fix CO_2 are
set forth in Table I below.

TABLE I

Chemical Compounds Useful for Chemically "Capturing" (or "Fixing") the Electrons, Hydrogen Ions and/or Carbon Dioxide Produced by the PDEC Invention

<u>No.</u>	<u>Feed Chemical</u>	Feed Chemical Structure(s). (NOTE: mixtures and blends of these materials are also effective)	Product from Reduction by Electrons with Hydrogen ions (additional similar products may be expected in many cases, therefore the compound(s) shown are representative but not necessarily all inclusive of the products expected. Specific electrochemical reduction conditions, such as electrode material, concentrations, pH, temperature, etc. will affect which product forms and the relative amounts of the products formed). (NOTE 1)	Product from Reduction by Electrons with Hydrogen ions including capture of carbon dioxide (additional similar products may be expected in many cases, therefore the compound(s) shown are meant to be representative but not necessarily all inclusive of the products expected. Specific electrochemical reduction conditions, such as electrode material, concentrations, pH, temperature, etc. will affect which product forms and the relative amounts of the products formed). (NOTE 1)
1	Sorbic Acid	$\text{CH}_3\text{CH}=\text{CHCH}=\text{CHCOOH}$, and the like.	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}=\text{CHCOOH}$ And/or, $\text{CH}_3\text{CH}=\text{CHCH}=\text{CHO}$	$\text{CH}_3\text{CH}(\text{COOH})\text{CH}_2\text{CH}=\text{CHCOOH}$ And/or, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}=\text{CHCOOH}$
2	Tocopherol derivatives (Vitamin E and similar compounds)	2R)-3,4-dihydro-2,8-dimethyl-2-[(4R,8R)-4,8,12-trimethyltridecyl]-2H-1-benzopyran-6-ol (or 8-methyltocol), and the like.	Same compound but with opened and chemically reduced ether ring (just the aromatic ring remaining)	Same compound but with opened and chemically reduced ether ring (just the aromatic ring remaining), and with one phenolic hydroxyl group replaced by a carboxyl group on the aromatic ring (ortho to the alkyl side chain).

3	D-Mannose	HOCH ₂ (HCOH) ₄ CHO isomer (in open or ring, pyranose and/or furanose form), and the like.	HOCH ₂ (HCOH) ₄ CH ₂ OH isomer	HOCH ₂ (HCOH) ₄ CH ₂ OH isomer carboxylated at one or more places along the hexose chain produced via a olefinic intermediate, for example HOCH ₂ (HCOH) ₃ (COH(COOH))CH ₂ OH.
4	Fructose	HOCH ₂ C(=O)(CHOH) ₃ CH ₂ OH isomer (in open or ring, pyranose and/or furanose hemiacetal, form), and the like.	Sorbitol and/or, Mannitol, i.e. HOCH ₂ C(=O)(CHOH) ₃ CH ₂ OH isomers with the other reduced hexose sugars.	HOCH ₂ (HCOH) ₄ CH ₂ OH isomer carboxylated at one or more places along the hexose chain produced via a olefinic intermediate, for example HOCH ₂ (HCOH) ₃ (COH(COOH))CH ₂ OH.
5	Aldotetroses	HOCH ₂ (HCOH) ₂ CHO (e.g. erythrose, threose, and the like.)	Reduced tetroses	Aldopentoses and reduced pentoses, straight chain and branched with a carboxylate group(s), e.g. carboxylated allose, altrose, glucose, mannose, gulose, idose, galactose, talose.
6	Aldopentoses	HOCH ₂ (HCOH) ₃ CHO (in open ring or ring form, i.e. furans, e.g. ribose, arabinose, xylose, lyxose, and the like.)	Reduced pentoses	Aldohexoses and reduced hexoses, straight chain and branched with a carboxylate group(s).
7	Ketotriose	Dihydroxyacetone (HOCH ₂ C(=O)CH ₂ OH), and the like.	HOCH ₂ CHOHCH ₂ OH (glycerin)	Carboxylated glycerin (e.g. HOCH ₂ C(COOH)OHCH ₂ OH)
8	Ketotetrose	HOCH ₂ C(=O)CHOHCH ₂ OH (one or more isomers), and the like.	Reduced tetrose	Aldopentoses and reduced pentoses, straight chain and branched with a carboxylate group(s), e.g. carboxylated allose, altrose, glucose, mannose, gulose, idose, galactose, talose.
9	Ketopentose	HOCH ₂ C(=O)(CHOH)CH ₂ OH (one or more isomers), and the like.	Reduced pentose	Aldohexoses and reduced hexoses, straight chain and branched with a carboxylate group(s).
10	Aldotriose	HOCH ₂ CHOHCHO (e.g. glyceraldehyde, and the like.)	Reduced triose	Aldotetroses and reduced tetroses, straight chain and branched with a carboxylate group(s).

11	Carbonic acid	H ₂ CO ₃ , and the like.	Formic acid (HCOOH), methanol (CH ₃ OH)	Oxalic acid and its salts (HOOC-COOH)
12	Lactic acid	CH ₃ CHOHCOOH, and the like.	CH ₃ CHOHCHO and/or CH ₃ CHOHCH ₂ OH	For example, CH ₃ CHOHC(=O)COOH and/or CH ₃ CHOHCH ₂ OHCOOH
13	Levulinic Acid	CH ₃ C(=O)CH ₂ CH ₂ COOH, and the like.	CH ₃ CHOHCH ₂ CH ₂ COOH and/or CH ₃ CHOHCH ₂ CH ₂ CHO	Carboxylated and chemically reduced levulinic acid.
14	Aliphatic aldehydes	RCHO where R = H, alkyl, and the like. For example, 1,3,5-trioxane {cyclic-(CH ₂ O) ₃ }, or cyclic-(CRR'O) ₃ , where R and R' = H, alkyl, and/or aryl, and where R and R' do not need to be the same.	Aliphatic alcohols in acidic tendency to yield alkyl alcohols (same for R-Ethyl where acetaldehyde and possibly, depending on conditions, 2,3-butanediol with high overpotential cathode and acidic medium; Isobutyraldehyde yields isobutane, isobutene, and isobutyl alcohol based on cathode and temperature.	Alpha-carboxylated alcohols, e.g. CH ₃ OH gives HOCH ₂ COOH
15	Vanillin	m-methoxy, p-hydroxy benzaldehyde acid, and the like.	m-methoxy p-hydroxy benzyl alcohol	Carboxylated m-methoxy p-hydroxy benzyl alcohol
16	Oxalic acid	HOOC-COOH, and the like.	OHC-CHO and/or HOOC-CHO, further reduction gives tartaric acid in acid medium); T greater than 40 C yields glycolic acid	Polycarbonate esters and/or HOOC-C(=O)COOH
17	Naphthalene	C ₁₀ H ₈ , and the like.	Hydrogenated naphthalene	Reduced and carboxylated naphthalene.
18	Diphenylacetylene and numerous other triple and/or double bond - containing organic compounds, conjugated with an aromatic ring structure.	Φ -C \equiv C- Φ (double bond feed material would be Φ -CH=CH- Φ where H could be substituted with aliphatics or other moiety.) (Φ indicates phenyl or other aromatic ring).	Cis or Trans Φ -CH=CH- Φ and/or Φ -CH ₂ CH ₂ - Φ	Φ -CH(COOH)CH(COOH)- Φ , and Φ -C(COOH)=C(COOH)- Φ type compounds (including the product cyclized).

19	Phthalimides (e.g. phthalimide) (Hydroxyphthalimide and N-methylphthalimide also work)	Phthalimide, and the like.	Anion of phthalimide	Carboxylated phthalimide
20	Azoxybenzenes (e.g. Azoxybenzene)	Azoxybenzene ($\Phi-N=N(O)-\Phi$), and the like.	$\Phi-N=\Phi$	$\Phi-N(COOH)-N(COOH)-\Phi$
21	m-Nitrophenol (o- and p- also work)	m-Nitrophenol, and the like.	p-hydroxy aniline	(N, N-dicarboxy)- p-hydroxy aniline
22	2,6-Dinitrotoluene	2,6-Dinitrotoluene, and the like.	2,6-diaminotoluene (also the monoamino nitrotoluene)	(N,N,N',N'-tetracarboxy)- 2,6-diaminotoluene
23	Chloropicrin	O ₂ N-CCl ₃ , and the like.	With Pt cathode yields dechlorinated methylhydroxylamine; with Pb cathode yields methylamine	(N,N-dicarboxy) methylamine
24	Nitramines (e.g. Nitramine)	H ₂ NNO ₂ , and the like.	Hydrazine (H ₂ N-NH ₂)	(N,N-dicarboxy) hydrazine
25	m-Nitrobenzaldehyde	m-Nitrobenzaldehyde, and the like.	(N,N'-m-benzaldehyde) azoxybenzene, m-(CHO)- Φ -N(COOH)-N(COOH)- Φ - m-(CHO), and the corresponding benzyl alcohol with further reduction, i.e. m-(CH ₂ OH)- Φ -N(COOH)-N(COOH)- Φ - m-(CH ₂ OH),	m-(CHO)- Φ -N(COOH)-N(COOH)- Φ - m-(CHO) and/or m-(CH ₂ OH)- Φ -N(COOH)-N(COOH)- Φ - m-(CH ₂ OH)
26	Aliphatic Ketones (e.g. Acetone, Methyl Ethyl Ketone, etc.)	R-C(=O)-R', and the like.	R-CHOH-R'	Carboxylated and electrochemically reduced aliphatic ketones, e.g. R-CH(COOH)CHOHR' (notice that "R" has one less carbon than the parent compound)

27	Cuminaldehyde	p-isopropyl benzaldehyde, and the like.	yields hydro- and isohydrocuminoin and/or p-isopropyl benzyl alcohol	Carboxylated and electrochemically reduced p-isopropyl benzaldehyde, e.g. carboxylated hydro- and isohydrocuminoin and/or p-isopropyl benzyl alcohol.
28	Salicylaldehyde	o-hydroxy benzaldehyde, and the like.	o-hydroxy benzyl alcohol	Carboxylated and electrochemically reduced o-hydroxy benzaldehyde, e.g. o-hydroxy benzyl alcohol
29	p-Acetamido-benzaldehyde	p-Acetamido-benzaldehyde, and the like.	with Hg cathode yields 4,4'-bis-p-acetamidohydrobenzoin	Carboxylated p-Acetamido-benzaldehyde, e.g. carboxylated 4,4'-bis-p-acetamidohydrobenzoin
30	Furfural	Furfural, (furan ring-CHO), and the like.	With Pb cathode yields a mixture of hydrofuroin and isohydrofuroin (e.g. furan ring - CH ₃ and/or hydrofuran ring-CH ₃).	Carboxylated and electrochemically reduced furfural, e.g. carboxylated hydrofuroin and isohydrofuroin.
31	p-Aminoaceto-phenone	p-Aminoaceto-phenone, and the like.	2,3-bis(p-aminobenzo)-2,3-butanediol	Carboxylated and electrochemically reduced p-Aminoaceto-phenone, e.g. 2,3-bis(p-aminobenzo)-2,3-butanediol, α -keto/hydroxy (p-amino)acetophenone
32	p-Hydroxyaceto-phenone	p-Hydroxyaceto-phenone, and the like.	2,3-bis(p-hydroxybenzo)-2,3-butanediol or 1-(p-hydroxybenzene) ethanol	Carboxylated and electrochemically reduced p-Hydroxyaceto-phenone
33	Phenylacetic Acid	Φ CH ₂ COOH, and the like.	Φ CH ₂ CH ₂ OH	Carboxylated and electrochemically reduced phenylacetic acid
34	m-Nitrobenzoic Acid (or ortho isomer)	m-Nitrobenzoic Acid (or ortho isomer), and the like.	m-amino benzyl alcohol	Carboxylated and electrochemically reduced m-nitrobenzoic acid (or ortho isomer)
35	3-Hydroxybenzoic Acid	3-Hydroxybenzoic Acid, and the like.	3-Hydroxybenzyl alcohol	Carboxylated and electrochemically reduced 3-hydroxybenzoic acid
36	2-Carboxy-benzaldehyde	2-Carboxybenzaldehyde, and the like.	Hydrodiphthalyl and phthalide and/or 2-carboxybenzyl alcohol	Carboxylated and electrochemically reduced 2-Carboxybenzaldehyde

37	β -keto esters	e.g. acetoacetic acid, butylacetoacetic acid, isobutylacetoacetic esters, and the like.	Yields the hydrocarbon (e.g. butane from acetoacetic acid. Bbutylacetoacetic acid with Pb cathode yields n-octane; isobutylacetoacetic ester yields octane)	Carboxylated and electrochemically reduced β -keto esters
38	N-mono and di Methyl- α -phenyl-acetamide	N,N-dimethyl- α -phenyl-acetamide and/or N-Methyl-2-phenylacetamide, and the like.	Yields N-methyl- β -phenylethylamine, or N,N-dimethyl- α -phenylacetamide, respectively. Pb cathode yields the corresponding amine.	Carboxylated amine (amide) derivatives are produced of N-methyl- β -phenylethylamine, or N,N-dimethyl- α -phenylacetamide, respectively. Produces one or two carboxylates/amine N.
39	Cyclic Imides	e.g. succinimides (e.g. N-H, N-methyl-, N-ethyl-, N-isopropyl-, and N-phenyl, and the like.)	2-pyrrolidones (e.g. N-H, N-methyl-, N-ethyl-, N-isopropyl-, and N-phenyl 2-pyrrolidones)	N-carboxylated 2-pyrrolidones.
40	Xanthine and/or Theophyllin	Xanthine and/or Theophyllin, and the like.	Hydrogenated Xanthine and/or Theophyllin	Carboxylated and hydrogenated Xanthine and/or Theophyllin
41	Aromatic halogenated acids	e.g., pentafluorobenzoic Acid; 3,5-Dibromo-2-Hydroxybenzoic Acid; or 5-Chloro-2-Hydroxybenzoic Acid, and the like.	Yields 2,3,5,6-tetrafluorobenzoic acid; with high potentials (>-1.30V), yields pentafluoro- and tetrafluorobenzyl alcohols. With Pb or Hg cathode and T below 30 C yields 3,5-dibromo-2-hydroxybenzyl alcohol. With Pb or Hg cathode and T below 30 C yields 5-chloro-2-hydroxybenzyl alcohol.	NA
42	α - and β -unsaturated and Aromatic Esters	e.g. Methyl-, Ethyl-, Isopropyl-Benzoates, and the like.	Hydrogenation reduces carbonyl to CH ₂ group, leaving other O as ether, aldehyde or alcohol. Terminal alkyl group, if reduced off, form low molecular weight alcohols (MeOH, EtOH, and iPrOH)	Carboxylated cabanion intermediates formed during electrochemical hydrogenation reaction.

43	Aromatic Carboxylic Acids	e.g. Benzoic Acid, substituted benzoic acids, and the like.	<u>Benzyl alcohol</u> , $\Phi\text{CH}_2\text{OH}$. <u>Dimer</u> , $[\Phi-(\text{C}=\text{O})-(\text{C}=\text{O})\Phi]$.	Carboxylated carbanion intermediates formed during electrochemical hydrogenation reaction.
44	Phenyl Benzoate Esters	e.g. benzyl benzoate, ethyl o-chloro benzoate, m-bromobenzoate, and the like.	The electrochemical reduction-hydrogenation of the invention yields the respective ethers, for example $\Phi-\text{OCH}_2\Phi$ for benzyl benzoate feed $[\Phi-\text{OC}(=\text{O})\Phi]$.	Carboxylated carbanion intermediates formed during electrochemical hydrogenation reaction of the aromatic rings and/or the adjoining methylene linkage of the product ether.
45	Phthalate Esters	Monoethyl Phthalate, Diethyl Phthalate, and the like.	The electrochemical reduction-hydrogenation of the invention yields the corresponding lactone.	Carboxylated carbanion intermediates formed during electrochemical hydrogenation reaction of the aromatic rings and/or the adjoining methylene linkage of the product lactone.
46	Benzamides ($\Phi-\text{C}(=\text{O})\text{NRR}'$) where R and R' are H, alkyl and do not have to be the same.	e.g. Benzamide with and/or without N-substitution, and the like.	The electrochemical reduction-hydrogenation of the invention yields the respective benzylamine ($\Phi\text{CH}_2\text{NH}_2$) where $\text{R}=\text{R}'=\text{H}$. N,N-disubstitution favors amine formation and thioamides follow same reduction. N-substituted benzamides form benzyl alcohol and an amine.	Carboxylated carbanion intermediates formed during electrochemical hydrogenation reaction of the aromatic rings and/or the adjoining methylene linkage of the product amine, and carboxylation of the product amine (up to three carboxylates per amine if R and R' are both H).
47	Nitriles of the Type $\text{XC}_6\text{H}_4\text{CN}$ or $\text{XC}_6\text{H}_3\text{N}$ with X = H, p-COOH, p-SO ₂ NH ₂ , or m-SO ₂ NH ₂ , and the like.	e.g. 2-cyanopyridine, or 4-cyanopyridine, Phthalonitrile and the like.	The electrochemical reduction-hydrogenation of the invention yields the respective aromatic ring, with the original substituents, and free cyanide (as the ion or as HCN).	Carboxylated carbanion intermediates formed during electrochemical hydrogenation reaction of the aromatic rings. In addition, the CO ₂ is captured by the cyanide ion to form carbamates and urea derivatives.

48	Aromatic aldehydes ($X\Phi\text{CHO}$, where X represents one or more substituents)	Benzaldehyde, ΦCHO , and the like.	With Ni, Pt, Fe, or Cu cathodes yields benzyl alcohol ($\Phi\text{CH}_2\text{OH}$). Under certain conditions yields a blend of benzyl alcohol, stilbene, and benzene. In alkaline medium yields hydro- and isohydrobenzoin	Carboxylated carbanion intermediates formed during electrochemical hydrogenation reaction of the aromatic rings.
49	Mannich Bases	e.g. p-Acetamido- ω -dimethylamino-propionophenone [$p(\text{H}_2\text{NC}(=\text{O})-\Phi-\text{C}(=\text{O})\text{CH}_2\text{CH}_2\text{NRR}'$, where R and R'=H, alkyl, aryl and do not have to be the same], and the like.	The electrochemical reduction-hydrogenation of the invention yields the respective dimer, e.g. for the example given, $p(\text{H}_2\text{NC}(=\text{O})-\Phi-\text{CX}(\text{OH})\text{CH}_2\text{CH}_2\text{NRR}'$ where X signifies the link to the group for the other half of the dimer.	Carboxylated carbanion intermediates formed during electrochemical hydrogenation reaction of the aromatic rings, and/or carboxylation of the amine groups, including the amide N if it is reduced to the amine.
50	bi- or tri-cyclic α -Aminoketones	e.g. 7-keto-1-azabicyclo 6.4.0 dodecane, and the like.	Bicyclic, non-aromatic ring system is opened at the N-C bridging bond to form one large (12 member) ring.	Carboxylated carbanion intermediates formed during electrochemical hydrogenation reaction. Carboxylation of the amine (formation of mono and bis carboxylates/carbamates).
51	1-Ethyl-4-Carboxypyridinium ion, and the like	p-HOOC-pyN-Et, and the like.	The electrochemical reduction-hydrogenation of the invention yields the respective aldehyde and/or alcohol.	Carboxylated carbanion intermediates formed during electrochemical hydrogenation reaction reducing the carboxylate to the aldehyde and/or to the alcohol. Electrochemical reduction of the py ring yields the carbanion.
52	N-Phenyl-4-Pyridinecarboxamide, and the like.	N-Phenyl-4-Pyridinecarboxamide, and the like.	The electrochemical reduction-hydrogenation of the invention yields the respective alcohol and amine mixture.	Carboxylated carbanion intermediates formed during electrochemical hydrogenation reaction of the aromatic rings, and/or carboxylation of the amine group(s) of the reduced compound.

53	Acetylenes (R-C≡C-R', where R and R' can be H, alkyl, aryl and mixtures thereof.	H-C≡C-H, and the like.	The electrochemical reduction- hydrogenation of the invention yields the respective alcohol, i.e. ethanol in the case of acetylene.	Carboxylated carbanion intermediates formed during electrochemical hydrogenation reaction of the feed compound.
54	Imino Ether Hydrochlorides	Imino Ether Hydrochlorides (RR'C=N-R''*HCl), and the like.	The electrochemical reduction- hydrogenation of the invention yields the respective amine, i.e. RR'CHNH-R'' for the example.	Carboxylated carbanion intermediates formed during electrochemical hydrogenation reaction of the aromatic rings, and/or carboxylation of the amine group(s) of the reduced compound.
55	Ethyl Esters of Fumaric, Tartaric, and Succinic Acids	e.g. Ethyl Succinate, and the like.	The electrochemical reduction- hydrogenation of the invention yields the respective alcohol.	Carboxylated carbanion intermediates formed during electrochemical hydrogenation reaction.
56	Pyridine-2- Carboxylic Acid	Pyridine 4-, Imidazole-2-, and Thiazole-2-Carboxylic Acid, and the like.	The electrochemical reduction- hydrogenation of the invention yields the respective aldehyde and/or alcohol.	Carboxylated carbanion intermediates formed during electrochemical hydrogenation reaction of the aromatic rings, and/or carboxylation of the amine group(s) of the reduced compound.
57	Methyl 2- Naphthoate (Methyl 1-naphthoate also works)	Methyl 2-Naphthoate, Methyl 1- naphthoate, and the like.	The electrochemical reduction- hydrogenation of the invention yields the respective 2-naph- thalenemethanol, a mixture of diastereomeric pinacols, methyl 1,2- and 1,4-dihydro-2- naphthoates (under same conditions yields methyl 1,4- dihydro-1-naphthoate dimer, di-1- naphthylglyoxal, and 1- naphthalenemethanol.	Carboxylated carbanion intermediates formed during electrochemical hydrogenation reaction of the aromatic rings.

58	Lactones	e.g. D-Ribone-gamma-Lactone, and the like.	The electrochemical reduction-hydrogenation of the invention yields the respective reduction of the carbonyl of the lactone to the corresponding alcohol, for the example, hydroxyaldehydes (D-Ribone-gamma-lactone yields D-ribose, i.e. HOCH ₂ CHX(CHOH) ₃ OX, where "X" designates the lactone intramolecular linkage.	Carboxylated carbanion intermediates formed during electrochemical hydrogenation reaction.
59	Thioesters	E.g. containing -C(O)SR, -C(S)OR, and/or -C(S)SR functions, and the like.	The electrochemical reduction-hydrogenation of the invention yields the respective reduction of the thioesters to their corresponding alcohols and hydrogen sulfides/mercaptans. The toxicity and odor of such products limit the utility of thioester raw materials to contained processes and away from human exposure.	The electrochemical reduction-hydrogenation of the invention yields the respective stable radical anions, under aprotic conditions, which are then active towards electrophiles, e.g. CO ₂ fixation.
60	Pyridine-4-Thiocarboxamide	Pyridine-4-Thiocarboxamide [p-py-C(=S)NH ₂], and the like.	The electrochemical reduction-hydrogenation of the invention yields the respective amine, p-py-CH ₂ NH ₂ and H ₂ S.	Carboxylated carbanion intermediates formed during electrochemical hydrogenation reaction of the aromatic rings, and/or carboxylation of the amine group(s) of the reduced compound.

61	Acyl Hydrazides	e.g. 4-Pyridinecarboxylic Acid Hydrazide ($\text{NH}_2\text{NHC}(=\text{O})-(p\text{-py})$), hydrazides of heterocyclic carboxylic acids, and the like.	The electrochemical reduction- hydrogenation of the invention yields 4-Pyridinecarboxamide which further reduces to the aldehyde, then to the alcohol. Hydrazides of heterocyclic carboxylic acids behave analogously.	Carboxylated carbanion intermediates formed during electrochemical hydrogenation reaction of the aromatic rings, and/or carboxylation of the amine group(s) of the reduced compound.
62	alpha,beta- Unsaturated Nitriles	$\text{R}-\text{CH}=\text{CHCN}$, and the like.	The electrochemical reduction- hydrogenation of the invention yields, under non-acidic conditions, hydrodimerization	Carboxylated carbanion intermediates formed during electrochemical hydrogenation reaction of the aromatic rings, and/or carboxylation of the amine group(s) of the reduced compound.
63	Substituted Nitrobenzenes, $\text{X}\Phi\text{NO}_2$	E.g. $o\text{-N}(\text{CH}_3)_2\Phi\text{NO}_2$, $o\text{-COCH}_3\Phi\text{NO}_2$, $o\text{-OCH}_3$, and/or $o\text{-CH}_3\Phi\text{NO}_2$, and the like.	The electrochemical reduction- hydrogenation of the invention yields the corresponding nitroso aromatics, and further reduction yields the amines.	Carboxylated carbanion intermediates formed during electrochemical hydrogenation reaction of the aromatic rings, and/or carboxylation of the amine group(s) of the reduced compound.
64	Azobenzenes, including substituted azobenzenes, $\text{R}\Phi\text{-N}=\text{N}-\Phi\text{R}'$	$\Phi\text{-N}=\text{N}-\Phi$, and the like.	The electrochemical reduction- hydrogenation of the invention yields the corresponding substituted hydrazines, i.e. $\text{R}\Phi\text{-NHNH}-\Phi\text{R}'$.	Carboxylated carbanion intermediates formed during electrochemical hydrogenation reaction of the aromatic rings, and/or carboxylation of the amine group(s) of the reduced compound.
65	Nitroaniline, substituted nitroanilines, and the like	e.g. m-Nitroaniline, o-Nitroaniline, and/or p-Nitroaniline, and the like.	The electrochemical reduction- hydrogenation of the invention yields the corresponding amines.	Carboxylated carbanion intermediates formed during electrochemical hydrogenation reaction of the aromatic rings, and/or carboxylation of the amine group(s) of the reduced compound, e.g. $\text{R}\Phi\text{-N}(\text{COOH})$, where $\text{R}=\text{aniline}$. Carboxylation of both amine groups can occur, which builds substantial capacity for CO_2 fixation.

66	Nitro-aliphatics, RNO ₂	Nitromethane, nitroethane, nitropropane, the nitro paraffins, and the like.	The electrochemical reduction- hydrogenation of the invention yields the corresponding alkyl hydroxylamines, e.g. methylhydroxylamine, ethylhydroxylamine, propylhydroxylamine, and the like. Further reduction yields the amine Hydrazine	Carboxylated carbanion intermediates formed during electrochemical hydrogenation reaction of the carbon(s) of the parent compound(s), and/or carboxylation of the amine group(s) and/or the O atoms of the N- OH groups of the hydroxylamine.
67	Nitrosamines	E.g., nitrosamine, and the like.		Carboxylated amines, e.g. H ₂ N-N(COOH) ₂ and the like.
68	Benzalanilines	E.g., benzalaniline (RΦ-N=CH- ΦR'), and the like.	RΦ-NH-CH ₂ -ΦR'	Carboxylated carbanion intermediates formed during electrochemical hydrogenation reaction of the carbons, and/or carboxylation of the amine group(s) i.e. RΦ-N(COOH)- CH(COOH)-ΦR', where double carboxylation is shown, and where CO ₂ addition to the aromatic rings can also sorb more CO ₂ after carbanion generation.
69	Glyoxylic Acid	OHC-COOH, and the like.	The electrochemical reduction- hydrogenation of the invention yields dimers, i.e., with Fe, Ni, or Ag cathode, tartaric acid (HOOCCHOHCHOHCOOH); and, with Pb, Cd, or Hg, yields succinic acid, HOOCCH ₂ CH ₂ COOH.	Carboxylated carbanion intermediates formed during electrochemical hydrogenation reaction of the carbon(s) of the parent compound(s).
70	Substituted cycloparaffin ketones and/or Aromatic Aldehydes	E.g. cyclopentanone, cyclohexanone, benzaldehyde, and the like.	The electrochemical reduction- hydrogenation of the invention yields dimers, e.g. for cyclopentanone, the dimer cyclic- C ₄ H ₈ C(H)(OH)- (HO)(H)cyclicC ₄ H ₈ is obtained.	Carboxylated carbanion intermediates formed during electrochemical hydrogenation reaction of the carbon(s) of the parent compound(s).

71	p-Dimethylamino-benzaldehyde	p-Dimethylamino benzaldehyde, and the like.	(p-(CH ₃) ₂ N)- Φ -CHOHCHOH- Φ - (p-(CH ₃) ₂ N)	Carboxylated carbanion intermediates formed during electrochemical hydrogenation reaction of the carbon(s) of the parent compound(s).
72	p-Hydroxybenzaldehydes	p-Hydroxybenzaldehyde, and the like.	The electrochemical reduction-hydrogenation of the invention yields p-methyl phenol, and alkyl phenols in general.	Carboxylated carbanion intermediates formed during electrochemical hydrogenation reaction of the aromatic ring(s) and/or aldehyde. The formation of phenolic carbonates also form from the phenolate anion at alkaline pH.
73	Aromatic Ketones	E.g. benzophenone, Φ C(=O) Φ and the like.	The electrochemical reduction-hydrogenation of the invention, with high overpotential cathode and aqueous acidic medium, yields benzpinacolone; and with high or low (Fe, Ni, Cu) overpotential electrode in acetic-sulphuric medium, yields the pinacolone.	Carboxylated carbanion intermediates formed during electrochemical hydrogenation reaction of the aromatic ring(s) and/or aldehyde.
74	β -Aminopropiophenone	E.g., p-aminopropiophenone, p-Et- Φ -NH ₂ , and the like.	The electrochemical reduction-hydrogenation of the invention yields (p-Et- Φ)-C(OH)X-C(OH)X-(p- Φ NH ₂), where X is a connecting intramolecular t-butyl group, one X bonding to one of the t-butyl methyl groups, and the other X to another methyl group of the same t-butyl group, thereby creating a five membered ring.	Carboxylated carbanion intermediates formed during electrochemical hydrogenation reaction of the carbon(s) of the parent compound(s).
75	β -Acetyl Pyridine	m-acetyl pyridine, and the like.	(m-py)-C(OH)(CH ₃)-C(OH)(CH ₃)-(m-py)	Carboxylated carbanion intermediates formed during electrochemical hydrogenation reaction of the aromatic ring(s) and/or ketone.

76	Formic Acid	HCOOH, and the like.	The electrochemical reduction- hydrogenation of the invention yields formaldehyde at low current density or methanol at high current density	Carboxylated carbanion intermediates formed during electrochemical hydrogenation reaction of the carbon(s) of the parent compound(s).
77	Halogenated benzoic Acids	E.g. m-chlorobenzoic acid, o- chlorobenzoic acid, p- chlorobenzoic acid, m- bromobenzoic acid and the like.	The electrochemical reduction- hydrogenation of the invention yields m-chlorobenzyl alcohol, o- chlorobenzyl alcohol and/or p- chlorobenzyl alcohol, m- bromobenzyl alcohol respectively.	Carboxylated carbanion intermediates formed during electrochemical hydrogenation reaction of the carbon(s) of the parent compound(s).
78	Salicylic Acid	Salicylic Acid (o-hydroxy benzoic acid), and the like.	The electrochemical reduction- hydrogenation of the invention yields o-hydroxybenzaldehyde, and the like.	Carboxylated carbanion intermediates formed during electrochemical hydrogenation reaction of the aromatic ring(s) and /or aldehyde.
79	Aromatic Dicarboxylic Acids	E.g. Phthalic Acid, and/or Isophthalic Acid, and the like.	The electrochemical reduction- hydrogenation of the invention yields phthalide. Isophthalic acid yields ω, ω' -dihydroxy-m-xylene)	Carboxylated carbanion intermediates formed during electrochemical hydrogenation reaction of the aromatic ring(s) and /or lactone.
80	α -Phenyl- acetamides	$\Phi\text{CH}_2\text{C}(=\text{O})\text{NRR}'$, and the like, where R and R' = H, alkyl, aryl and can be different.	The electrochemical reduction- hydrogenation of the invention yields $\Phi\text{CH}_2\text{CH}_2\text{NRR}'$.	Carboxylated carbanion intermediates formed during electrochemical hydrogenation reaction of the aromatic ring(s), and especially the product amine. Most preferred is the case where $\text{R}=\text{R}'=\text{H}$ since more CO_2 can be fixed (2-3/mole).
81	Diketopiperazines, isocyanuric acids, and the like.	E.g. diketopiperazine, (1,4-diaza- 3,6-dicarbonylcyclohexane, $\text{C}_4\text{H}_6\text{N}_2\text{O}_2$), and the like.	The electrochemical reduction- hydrogenation of the invention yields $\text{NH}_2\text{CH}_2\text{CH}_2\text{CNHO}$ and the like.	Carboxylated carbanion intermediates formed during electrochemical hydrogenation reaction of the carbon(s) of the parent compound(s), and especially the fixation of CO_2 by the product amine(s).

82	Barbituric Acid, and isocyanuric acids, and the like.	E.g. 5,5-diethylbarbituric acid (1,3-diaza-2,4,6-tricarbonyl cyclohexane), and the like.	The electrochemical reduction-yields reduction of one or more of the carbonyls present in the parent compound.	Carboxylated carbanion intermediates formed during electrochemical hydrogenation reaction of the carbon(s) of the parent compound(s), and especially the fixation of CO ₂ by the product amine(s).
83	Phenylacetic Acid	E.g. $\phi\text{CH}_2\text{COOH}$, R- $\phi\text{CH}_2\text{COOH}$, $\phi\text{CR}'\text{R}''\text{COOH}$ and the like, where R, R', and R'' can be different or the same, and consists of alkyl, aryl, H, halogen, pseudo halogen, alkoxide, and the like.	The electrochemical reduction-yields reduction of one or more of the carbonyls present in the parent compound to form the corresponding alcohols $\phi\text{CH}_2\text{CH}_2\text{OH}$	Carboxylated carbanion intermediates formed during electrochemical hydrogenation reaction of the aromatic ring(s) and methylene group(s).
84	Dimethyl Terephthalate	, and the like.	Hydrogenation reduces carbonyl to CH ₂ group, leaving other O as ether, aldehyde or alcohol on both sides of the molecule. Terminal alkyl group, if reduced off, form low molecular weight alcohols (MeOH, EtOH, and iPrOH)	Carboxylated carbanion intermediates formed during electrochemical hydrogenation reaction of the aromatic ring(s). Carboxylated carbanion intermediates formed during electrochemical hydrogenation reaction which capture and fix CO ₂ .
85	Phthalic Anhydride	Phthalic Anhydride, and the like.	The electrochemical reduction-yields phthalide (lactone) using monoethyl phthalate as substrate).	Carboxylated carbanion intermediates formed during electrochemical hydrogenation reaction of the aromatic ring(s). Carboxylated carbanion intermediates formed during electrochemical hydrogenation reaction which capture and fix CO ₂ .
86	Diesters of Terephthalate, furans, and/or thiophenes.	E.g. diethyl terephthalate, diethyl furan, and/or thiophene-2,5-dicarboxylate.	The electrochemical reduction-yields the aldehyde ester	Carboxylated carbanion intermediates formed during electrochemical hydrogenation reaction of the aromatic ring(s). Carboxylated carbanion intermediates formed during electrochemical hydrogenation reaction which capture and fix CO ₂ .

87	Adipate Esters	Dimethyl Adipate	The electrochemical reduction- hydrogenation of the invention yields n-hexane.	Carboxylated carbanion intermediates formed during electrochemical hydrogenation reaction which capture and fix CO ₂ , e.g. as HOOCCH ₂ CH ₂ CH ₂ CH ₂ CH ₂ COOH.
88	N-Alkylphthal- imides and Oxamides	E.g. N,N-Dimethylbenzamide [$\Phi C(=O)N(CH_3)_2$]	The electrochemical reduction- hydrogenation of the invention yields a blend of alcohols and amines, e.g. $\Phi CH_2N(CH_3)$, ΦCH_2OH , $HN(CH_3)_2$, etc.	Carboxylated carbanion intermediates formed during electrochemical hydrogenation reaction of the carbon(s) of the parent compound(s), the aromatic ring(s), and especially the fixation of CO ₂ by the product amine(s) to form carbamates and bicarbonate salts with quaternary ammonium ions, for example $(CH_3)_2N^+(COO^-)_2$, HCO_3^- , $(CH_3)_2N^+H(COO^-)$, HCO_3^- , etc.
89	Substituted Phthalamides	E.g. N-Phenylphthalimide	The electrochemical reduction- hydrogenation of the invention yields O-acetyl-2- hydroxymethylbenzanilide	Carboxylated carbanion intermediates formed during electrochemical hydrogenation reaction of the carbon(s) of the parent compound(s), the aromatic ring(s), and especially the fixation of CO ₂ by the product amine(s) to form carbamates and bicarbonate salts with quaternary ammonium ions.
90	Benzonitriles	E.g. R Φ CN, where R=any one or combination of a series of substituents where R= H, alkyl, aryl, etc.	The electrochemical reduction- hydrogenation of the invention yields solutions of relatively stable anion radicals.	Carboxylated carbanion intermediates formed during electrochemical hydrogenation reaction of the carbon(s) of the parent compound(s), the aromatic ring(s), and especially the fixation of CO ₂ by the product amine(s) to form carbamates and bicarbonate salts with quaternary ammonium ions.

91	1,5-Dinitro-naphthalene	1,5-Dinitro-naphthalene	The electrochemical reduction- hydrogenation of the invention yields 1,5-Diamino-naphthalene	Carboxylated carbanion intermediates formed during electrochemical hydrogenation reaction of the carbon(s) of the parent compound(s), the aromatic ring(s), and especially the fixation of CO ₂ by the product amine(s) to form carbamates and bicarbonate salts with quarternary ammonium ions.
92	Amino Ketones	E.g. p-Aminopropiophenone	The electrochemical reduction- hydrogenation of the invention yields $\text{pH}_2\text{N}-\Phi-\text{C}(\text{OH})\text{Et}-\text{C}(\text{OH})\text{Et}-\Phi-\text{NH}_2$.	Carboxylated carbanion intermediates formed during electrochemical hydrogenation reaction of the carbon(s) of the parent compound(s), the aromatic ring(s), and especially the fixation of CO ₂ by the product amine(s) to form carbamates and bicarbonate salts with quarternary ammonium ions.
93	α -Aminoketones	E.g. 1-Methyl-2-Ethyl-3-Piperidone	The electrochemical reduction- hydrogenation of the invention yields 1-Methyl-2-Propylpyrrolidine, 1-Methyl-2-Ethyl-3-Hydroxypiperidine, N-Methyl-Heptylamine, and 1-Methyl-2-Propyl-2-Pyrroline.	Carboxylated carbanion intermediates formed during electrochemical hydrogenation reaction of the carbon(s) of the parent compound(s), and especially the fixation of CO ₂ by the product amine(s) to form carbamates and bicarbonate salts with quarternary ammonium ions.
94	Cyclic amides	Morpholinone Series (benzene ring fused with a morpholine ring at the 1 and 2 positions, and the morpholine having a keto group at the 5 position.	The electrochemical reduction- hydrogenation of the invention yields 2-hydroxy-(N-acetyl) aniline, C ₈ H ₉ NO ₂ .	Carboxylated carbanion intermediates formed during electrochemical hydrogenation reaction of the carbon(s) of the parent compound(s), and especially the fixation of CO ₂ by the product amine(s) to form carbamates and bicarbonate salts with quarternary ammonium ions.

95	Ethyl 2-Thiazolecarboxylate	Ethyl 2-Thiazolecarboxylate (cyclic-C ₂ H ₂ NSC _c -COOEt), where C _c denotes the carbon of the ring containing the substituent group.	The electrochemical reduction- hydrogenation of the invention yields the ester of the parent compound reduced to an aldehyde, or further to the alcohol.	Carboxylated carbanion intermediates formed during electrochemical hydrogenation reaction of the carbon(s) of the parent compound(s), and especially the fixation of CO ₂ by the product amine(s) to form carbamates and bicarbonate salts with quaternary ammonium ions.
96	Imidic Esters	E.g. Ethyl Acetimidate (CH ₃ C(=NH)OEt)	The electrochemical reduction- hydrogenation of the invention yields EtNH ₂ plus EtOH.	Carboxylated carbanion intermediates formed during electrochemical hydrogenation reaction of the carbon(s) of the parent CO ₂ by the product amine(s) to form carbamates and bicarbonate salts with quaternary ammonium ions.
97	Stilbenes	E.g. Φ -CH=CH- Φ	The electrochemical reduction- hydrogenation of the invention yields carbanions and reduction to aliphatic linkages.	Carboxylated carbanion intermediates formed during electrochemical hydrogenation reaction of the carbon(s) of the parent compound(s), e.g. Φ - CH(COOH)-CH(COOH)- Φ .
98	p-Carboxyacetophenone	E.g. p HOOC- Φ -C(=O)R, where R= alkyl, aryl, and the like	The electrochemical reduction- hydrogenation of the invention yields pHOOC- Φ -C(OH)(R)- C(OH)(R)- Φ -pCOOH.	Carboxylated carbanion intermediates formed during electrochemical hydrogenation reaction of the carbon(s) of the parent compound(s).
99	Dialkyl Oxalates, ROOCCOOR where R=alkyl, and the like.	E.g. Diethyl Oxalate, EtOCCCOOEt	The electrochemical reduction- hydrogenation of the invention yields ethyl hemiacetal of ethyl glyoxylate.	Carboxylated carbanion intermediates formed during electrochemical hydrogenation reaction of the carbon(s) of the parent compound(s).
100	2-Alkyl substituted Acetoacetic Esters and beta-Diketones	E.g. Ethyl 2-Butylacetoacetate	The electrochemical reduction- hydrogenation of the invention yields 2,3-octanedione, CH ₃ C(=O)C(=O)(CH ₂) ₃ CH ₃	Carboxylated carbanion intermediates formed during electrochemical hydrogenation reaction of the carbon(s) of the parent compound(s).

101	Thiol Esters of Aromatic Acids	E.g. S-Benzoyl-L-cysteine [$\Phi C(=O)SCH_2CH(NH_2)COOH$]	The electrochemical reduction- hydrogenation of the invention yields L-cysteine, HSCH ₂ CH(NH ₂)COOH	Carboxylated carbanion intermediates formed during electrochemical hydrogenation reaction of the carbon(s) of the parent compound(s), and especially the fixation of CO ₂ by the product amine(s) to form carbamates and bicarbonate salts with quarternary ammonium ions.
102	N,N-Dimethyl and N,N-Diphenyl- substituted Aliphatic Amides	N,N-Dimethyl and N,N-Diphenyl- substituted Aliphatic Amides	The electrochemical reduction- hydrogenation of the invention yields the corresponding aminomethyl compounds	Carboxylated carbanion intermediates formed during electrochemical hydrogenation reaction of the carbon(s) of the parent compound(s), and especially the fixation of CO ₂ by the product amine(s) to form carbamates and bicarbonate salts with quarternary ammonium ions.
103	Ethyl Ester of Acetoacetic Acid	Ethyl Ester of Acetoacetic Acid	The electrochemical reduction- hydrogenation of the invention yields 4-aldopyridine or 4-methanol pyridine.	Carboxylated carbanion intermediates formed during electrochemical hydrogenation reaction of the carbon(s) of the parent compound(s), and especially the fixation of CO ₂ by the product amine(s) to form carbamates and bicarbonate salts with quarternary ammonium ions.
104	Anisaldehyde	E.g. p-Anisaldehyde)	The electrochemical reduction- hydrogenation of the invention yields hydro- and isohydroanisoin	Carboxylated carbanion intermediates formed during electrochemical hydrogenation reaction of the carbon(s) of the parent compound(s), and especially the fixation of CO ₂ by the product amine(s) to form carbamates and bicarbonate salts with quarternary ammonium ions.

105	Aliphatic Nitriles	E.g. Heptanecarbo-nitrile and/or cycloheptane-carbonitrile	The electrochemical reduction-yields cleavage of the C-CN bonds.	Carboxylated carbanion intermediates formed during electrochemical hydrogenation reaction of the carbon(s) of the parent compound(s), and especially the fixation of CO ₂ by the product amine(s) to form carbamates and bicarbonate salts with quarternary ammonium ions.
106	Aromatic Nitriles	E.g., p-RCOC ₆ H ₄ CN with R = H or CH ₃	The electrochemical reduction-yields the corresponding benzylamine.	

NOTES:

1. Notice that the word "reduced" in the above table signifies a compound that was prepared using the invention by adding at least two electrons, and usually two H⁺ ions to the parent or "feed" compound.
2. All acids can be present as the parent acid or the salt of the acid with the cation(s) being one or more of the following: K⁺, Na⁺, Ca²⁺, Mg²⁺, Zn²⁺, Li⁺, NH₄⁺, NR₄⁺ (where R= any combination of alkyl, aryl, H, etc.) aquo ions.

References:

1. "Electrochemistry in Biology and Medicine" T. Shedlovsky, Ed., John Wiley and Sons Publ., (New York, NY), 1955, and references therein.
2. "Sugar Chemistry " by R.S. Shallenberger and G.G. Birch, The AVI Publ. Co. (Westport, CT), 1975 , and references therein.
3. "Synthetic Organic Electrochemistry" A.J. Fry, Harper & Row, Publ. (New York, NY), 1972, and references therein.
4. "Organic Electrode Processes" by M.J. Allen , Reinhold Publ. (New York, NY), 1958, and references therein.
5. "Biochemistry" by R.H. Garrett and C.M. Grisham, Saunders College Publ. (New York, NY), 1995, and references therein..

6. "Modern Electrochemistry", Volumes I and II, J.O'M Bockris and A. K. N. Reddy, Plenum Press (New York, NY), 1977, and references therein.
7. Parker, E.A., and Sherlock, S., *Transactions of the Electrochemical Society*, Vol. 92 (1947) 343-368.
8. Wilson, C.L. and Kenneth, B.W., *Transactions of the Electrochemical Society*, Vol. 80 (1944) 139-150.
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13. Radical anions of activated olefins generated at the cathode react rapidly with CO₂ to produce succinic acid derivatives in the absence of water. This is described in full by Tysee, D.A. and Baizer, M.M., *The Journal of Organic Chemistry*, Vol. 39, No. 19 (1974) 2819-2823.
14. "Possible Reduction of Carbon Dioxide to Oxalates by Amalgams of Alkali Metals in Nonaqueous Media", v. a. TUSHNALOBOVA, v. a. Smirnov, and D. P. Semchenko (Novocherkassk Politekhn Inst. Im. Ordzhonikidze, Novocherkassk, USSR). *Chemical Abstracts*, Vol. 68, 1968, p 10698.

Additional references that may be used for this invention include:

- Parker, E.A., and Sherlock, S., *Transactions of the Electrochemical Society*, Vol. 92 (1947) 343-368.
- 5 ◦ Wilson, C.L. and Kenneth, B.W., *Transactions of the Electrochemical Society*, Vol. 80 (1944) 139-150.
- Shallenberger, R.S. and Birch, G.G., "Sugar Chemistry," The AVI Publishing Company, Inc, Westport, Connecticut, 1975.
- 10 • Baizer, M.N. and Lund, H., "Organic Electrochemistry," Second Edition, Marcel Dekker, Inc, New York.

And included references.

- 15 • Allen, M.J. "Organic Electrode Processes," Reinhold Publishing Corp, New York, 1958.
 - Use of carbon dioxide as a trapping agent for carbanions (see "Synthetic Organic Electrochemistry," Albert J. Fry, Harper & Row Publishers, New York): reduction of diphenylacetylene in the presence of CO₂ and H₂
 - 20 yields diphenylmaleic anhydride, diphenylfumaric acid, and meso-diphenylsuccinic acid.
 - Electrocarboxylation of various organic compounds including:
 - Aryl olefins
 - Acetylene
 - 25 ◦ Polynuclear hydrocarbons
 - Butadiene
 - Aromatic ketones
 - α,β – unsaturated aryl and aryl-substituted alkyl ketones
 - benzalaniline
 - 30 ◦ acrylonitrile
- these are reported by Tyssee, D.A. et al, *Tetrahedron letters*, No. 47 (1972) 4809-4812.

- Radical anions of activated olefins generated at the cathode react rapidly with CO₂ to produce succinic acid derivatives in the absence of water. This is described in full by Tysee, D.A. and Baizer, M.M., *The Journal of Organic Chemistry*, Vol. 39, No. 19 (1974) 2819-2823.

5

D. Preparation of Microfabrication Structures

3-D Cell Structure:

10 The manner in which individual photolytic surfaces (2-D constructs) are organized into a 3-D network is important for achieving DO yield that meets human physiological needs. A 3-D cell structure may be developed using any number of methods including fluid dynamics modeling, knowledge of semiconductor integrated circuit thin film fabrication techniques, optics, and system electronics and fabricated as a set of nanopatterned, stacked surfaces
15 (3-D construct). Although apparently complex, component arrays such as these are becoming increasingly common, with the appearance of "lab on a chip", "combinatorial chemistry", and "micro-technology chemical manufacturing" type devices. Such devices are derived from the evolving science of micro-fabrication
20 (μ FAB), and employ simple, yet robust, approaches used in the manufacture of integrated circuits for the semiconductor industry. Such μ FAB techniques can be used to produce the composite, high surface area, photolytically driven thin film coatings ("constructs") for this technology, as applied to the artificial lung device. Light may be distributed within the 3-D construct using micro-scale wave-guides,
25 and optimized to provide efficient photo-induction at all UV light/photoactive surface interface.

 The PDEC will be utilized as a three-dimensional flow-through device. As mentioned above, the selection of the 3-D structure will be dependent, in part, on fluid dynamics modeling of fluid (blood or other process liquid) flow across
30 the photoactive surface and within a confined space to determine the geometry and size. The 3-D device will contain micro-fabricated capillary mimicking structures/tubules to provide intimate and complete contact between the bulk liquid flow and the photoactive, oxygen production surfaces, as well as the

cathode/CO₂ fixation surface. The width of these channels/tubules may vary, but must be at least larger than the diameter of a red blood cell (~7µm) in the case of blood containing processes. The length of the tubes may also vary, and is dependent on the residence time required to fully oxygenate the fluid (blood). In the case of the artificial lung applications, it is anticipated that the width and length of the channels will be 10-100µm and 50-500µm, respectively. Figure 10 includes two possible geometries for the 3-D device.

Using micro fabrication, large surface areas are possible for the DO reaction surface. Additionally, the PAL 3-D device will possess numerous repeating structures. Interference lithography is the preferred method for fabricating periodic and quasi-periodic patterns that must be spatially coherent over large areas. It is a conceptually simple process where two mutually coherent beams interfere to produce a standing wave, which can be recorded in a photo-resistor. The spatial period of the standing wave can be as fine as half the wavelength of the interfering light, allowing the formation of structures on the order of 100 nm using UV light, or features as small as 30-40 nm using deep ultraviolet. Figures 11A - 11C show examples of nanostructures fabricated on silicon and polymer materials for diverse applications using variants of the interference photolithography technique.

Any other similar fabrication processes may also be utilized. For example, a unique process that utilizes a sacrificial bracing material to create 3-D microstructures such as waveguides, polarization elements, filters, ion exchange membranes, and microfluidic conduits, chambers, and valves may be used. A structure created using this process is illustrated in Figure 12. This microfabrication technique uses traditional photolithography with an epoxy material and the above-mentioned sacrificial material. The fabrication process results in a chemically, biochemically, mechanically, and thermally stable material. An important advantage of this technique is the ability to create fully three-dimensional structures having high aspect ratios.

The specific geometry of the individual tubules should be determined by the required durability, (bio)compatibility, and DO production rate. These structures may be stacked together into a space-efficient arrangement that will result in a compact device that is capable of producing oxygen at a high rate. Again, computational modeling and conventional optics design and optimization

techniques will allow the creation of a stacked construct that is optimized/efficient in regards to both fluid flow and light transport and utilization.

The goal of the stacking method is to obtain closely aligned surfaces where the photolytic reaction can take place with maximum catalytic efficiency and light utilization. The key aspect of this development will be to use directed
5 laser light most efficiently within a given volume of process liquid (blood).

The present invention is further described with reference to several examples set forth below.

10

Example 1

In this example, oxygen is produced and carbon dioxide is removed from stale air using water, C₃ or C₅ compounds and photolytic energy. Referring now to Figure 2, a PDEC cell 16 is used for the central reaction of producing oxygen in the anode compartment 100 and producing a C₆ compound, such as hexose
15 sugar, from carbon dioxide in the cathode compartment 102.

In this regard, stale air (high in CO₂ and low in O₂) 104 is first contacted with a liquid such as a recycled catholyte (e.g. aqueous phosphate with Mg²⁺ catalyst) in gas/liquid contactor 106 to convert the carbon dioxide into dissolved form in the liquid, normally CO₂ (aq), but could also be HCO₃⁻, H₂CO₃ and/or
20 CO₃²⁻. The gas/liquid contactor 106 can be in a counter flowing percolating bed, a micro-porous membrane, gas sparger, etc.

The dissolved carbon dioxide catalyst, glycerate, and pentose and the liquid then flow into the cathode compartment 102 of the PDEC cell 16. Pentose can also be contained in the contacting liquid catalyst. The pentose reacts with
25 the carbon dioxide converting it to glycerate or the equivalent. The glycerate is electrochemically reduced at the surface of the cathode 108. The surface of the cathode is preferably coated with a catalyst that facilitates the hydrogenation reduction reaction such as Pb, Cd, Ni, Pd and the like. The reaction then uses the hydrogen ions that migrate across the membrane 126 from the anode
30 compartment 110 to form a hexose sugar. The hexose sugar solution flows out of the cathode compartment 102 into a separator 112, where the liquid may be recycled and the hexose sugar placed in stores 114 or used as food for the crew, animals or microorganisms. For example the sugar-like compound, or

carbohydrate-like compound, or glycerate can be recovered by crystallization, micro-filtration, electrodeionization, and the like.

The anode compartment 100 comprises the oxygen-producing portion of PDEC cell 16. Electrolyte 128 such as NaCl brine, Na₂SO₄, K₂O₄, H₂SO₄, HCl, and the like flows into the anode compartment 100. The reaction of light with the photoactive surface 116 comprising a photolytic catalyst and a disproportionation catalyst generates charge separation, the positive portion of which reacts with the water present in the electrolyte to form oxygen and hydrogen ions. As mentioned above, the hydrogen ions migrate into the cathode compartment 102 for further reaction. The oxygen flows out of the anode compartment 100 dissolved in the electrolyte and optionally can be allowed to coalesce into O₂ bubbles. The dissolved oxygen and/or O₂ bubbles and brine flow to an oxygen degasser or gas permeation tube 118 where the two are separated. The electrolyte is recycled to the anode compartment 100 while the oxygen flows to the enclosed volume 120 for breathing by humans, animals, microorganisms or other uses. The oxygen may also be pressurized for later use.

Example 2

This example illustrates the production of oxygen and the reduction of CO₂ through the formation of a C₃ compound intermediary. Referring now to Figure 3, a PDEC cell 16 is used for the central reaction of producing oxygen and reducing the carbon dioxide obtained from the confined space 120. Stale air 104 is first contacted with a liquid such as aqueous brine containing a α -keto pentose containing a catalyst typically of mixtures of Mg²⁺/PO₄³⁻ electrolyte gas/liquid at contactor 106 to convert the carbon dioxide into dissolved form in the liquid. This contact at contactor 106 may be in a counter flowing circulating bed, a porous membrane, or in a percolating bed, etc. The dissolved carbon dioxide, e.g. now in the carbon dioxide laden electrolyte, is also contacted with the C₅ pentose obtained from stores 122, also containing a catalyst, e.g. rubisco type enzymatic catalyst or a derivative compound for this enzyme. In this manner the CO₂ and α -keto ribulose is converted to two C₃ glycerate molecules at C₃ formulator 124. The rubisco type reaction is discussed and disclosed in

reference by Garrett, Reginald et al; Biochemistry; Saunders College Publ.; pp. 720-721, (1995).

The dissolved C_3 compounds may then be ultra filtered to recover the enzyme and the filtrate flows to the cathode compartment 102 of the PDEC cell
5 16. The enzyme fraction is recycled. The enzyme may also be immobilized on a solid support or as easy-to-filter gel particles for ease of recovery/separation by means well known in the art of immobilized enzyme.

The surface of the cathode is preferably coated with a catalyst 124 that facilitates the C_3 to C_6 coupling reaction such as Ni, Pd, Pb, Cd, and the like to
10 form sugar like compounds. The cathode compartment 102 typically uses an electro-hydrodimerization PO_4^{3-} buffer at a pH of about 7 to 9 to form a hexose (C_6) sugar. The cathodic reaction also uses the hydrogen ions that migrate across the membrane 126 from anode compartment 100. The hexose sugar and electrolyte flow out of the cathode compartment into a separator 112, where
15 the liquid may be recycled and the hexose sugar placed in stores 114 or used as food for the crew, animals or microorganisms.

As in Example 1 above, the anode compartment 100 comprises the oxygen-producing portion of PDEC cell. Aqueous electrolyte 128 such as HSO_4 , Na_2SO_4 , NaCl brine, seawater, fermentation broth, etc. flows into the anode
20 compartment 100. In an additional benefit of the technology, the photolytic cell allows improved oxygenation of aerobic and facultative aerobic fermentations since the fiber optics arrangements can be used to disperse the oxygen uniformly and prolifically.

The reaction of light 114 with the photoactive surface 116 in the anode
25 compartment 100 generates charge separation, the positive portion of which reacts with the water present in the electrolyte to form oxygen and hydrogen ions. As mentioned above, the hydrogen ions migrate from the anode compartment 100, across the membrane 126, into the cathode compartment 102 for further reactive use. The oxygen flows out of the anode compartment
30 100 dissolved in the electrolyte and optionally can be allowed to coalesce into O_2 bubbles. The dissolved oxygen and/or O_2 bubbles and brine flow to an oxygen degasser 118 or gas permeation tube where the two are separated. The electrolyte 128 is recycled to the anode compartment 100 while the oxygen flows to the enclosed volume 120 for breathing by humans, animals,

microorganisms or other uses. The oxygen may also be pressurized for later use.

Other embodiments of the invention are illustrated in Figures 4 through 6. Figure 4 is a schematic of an embodiment of the invention showing details of a
5 rubisco-catalyzed reaction used to prepare a C_3 carbon intermediary for carbon dioxide removal. Figure 5 is a schematic of a more detailed embodiment of the invention showing the rubisco catalyzed reaction and the chemical steps in greater detail. Moreover, Figure 6 is a schematic of another embodiment of the invention wherein the carbon dioxide is reacted with the pentose directly in the
10 PDEC cell.

Additionally, it is important to note that when the optional membrane 126 is not used, appropriate consideration must be given to the reactions that may occur at the electrodes taking into consideration that mixing of components may occur. In some embodiments a separator that is not a cationionic membrane
15 may used that provides attenuated movement of materials.

Furthermore, Figures 7-9 show various embodiments of the invention incorporated into different environmental settings.

While the forms of the invention herein disclosed constitute presently preferred embodiments, many others are possible. It is not intended herein to
20 mention all of the possible equivalent forms or ramifications of the invention. It is to be understood that the terms used herein are merely descriptive, rather than limiting, and that various changes may be made without departing from the scope of the invention.

Having thus described the preferred embodiment, the invention is now claimed to be:

1. A photolytic apparatus for oxygenating and removing carbon dioxide from a confined volume area comprising:
a photolytic cell having an anode compartment with a photo-active surface having the ability to convert water to oxygen; and, a cathode
5 compartment having the ability to convert carbon dioxide and hydrogen to a solid or liquid medium; and
a light source for providing light photons to said photolytic cell and activating the photo-reactive surface.
2. The apparatus of claim 1, wherein said photo-reactive surface comprises a light-activated catalyst.
3. The apparatus of claim 2, wherein said light activated catalyst is a metal oxide catalyst comprising anatase (TiO_2), WO_3 or ZnO , combinations thereof, with or without performance enhancing dopants.
4. The apparatus of claim 1, wherein said light source is an ultraviolet light at 350-500 nm.
5. The apparatus of claim 2, wherein said light-activated catalyst converts, when photolytically irradiated, water to hydrogen ions, electrons and active oxygen.
6. The apparatus of claim 5, wherein said active oxygen formed during photolysis is hydrogen peroxide or other forms of oxygen gas precursors.
7. The apparatus of claim 5, wherein said electrons generated during photolysis are then electrically conducted away to avoid reversal of the reaction.
8. The apparatus of claim 5, wherein said active oxygen formed during photolysis is converted by a disproportionation catalyst into dissolved oxygen.

9. The apparatus of claim 8, wherein said disproportionation catalyst is MnO_2 .
10. The apparatus of claim 1, wherein the carbon dioxide and hydrogen are converted to a carbonate solid.
11. The apparatus of claim 1, wherein the hydrogen is reacted with a substrate to produce a non-gaseous substance.
12. The apparatus of claim 11, wherein the substrate is an electrochemically reducible compound.
13. The apparatus of claim 1, wherein the photo-reactive surface comprises a light transparent substrate and a photolytic coating.
14. The apparatus of claim 13, wherein said photolytic coating comprises a layer of a light activated catalyst which converts, when photolytically irradiated, water to hydrogen ions, electrons and active oxygen.
15. The apparatus of claim 14, wherein said photolytic coating further comprises a disproportionation catalyst which converts active oxygen to dissolved oxygen.
16. The apparatus of claim 1, wherein the anode compartment and the cathode compartment are separated by a membrane.
17. The apparatus of claim 16, wherein said membrane allows for the flow of hydrogen ions from the anode compartment to the cathode compartment.
18. The apparatus of claim 1, wherein the photolytic cell comprises a mesoporous material.

19. A photolytic apparatus for oxygenating and removing carbon dioxide and hydrogen gas in order to maintain a proper physiological environment comprising:

5 a photolytic cell having an anode compartment and a cathode compartment, a) said anode compartment having an inlet for receiving an aqueous solution, an anode conductor, a photo-reactive surface, and an outlet for transporting a dissolved oxygenated solution out of said anode compartment, wherein said photo-reactive surface has the ability, upon photo-activation, to convert water in an aqueous solution to dissolved oxygen, hydrogen ions and
10 electrons upon light activation; b) said cathode compartment having an inlet for receiving carbon dioxide, C₅ pentose, and a catalyst, a cathode conductor for converting hydrogen ions, carbon dioxide, C₅ pentose and catalyst to C₆ pentose, and an outlet for removing the C₆ pentose from the cell and any remaining reactants; and,

15 a light source for providing light photons to said photo-reactive surface to initiate a series of chemical reactions that results in dissolved oxygen generation in the anode compartment and C₆ pentose formation in the cathode compartment.

20. The apparatus of claim 19, wherein said light photo-reactive surface comprises a layer of a light activated photolytic catalyst.

21. The apparatus of claim 20, wherein said light activated photolytic catalyst is a metal oxide comprises TiO₂ (anatase), WO₃ or ZnO, or combination thereof.

22. The apparatus of claim 19, wherein said light source is an ultraviolet light at 350-500 nm.

23. The apparatus of claim 19, wherein said photo-reactive surface further comprises a disproportionation catalyst.

24. The apparatus of claim 19, wherein said photolytic cell comprises a transparent substrate and a photolytic coating comprising a first disposed layer of TiO₂ (anatase) and a second disposed layer of MnO₂.

25. The apparatus of claim 19, wherein said cell is constructed from mesoporous materials.
26. The apparatus of claim 23, wherein said disproportionation catalyst includes at least one of Fe^{II} , Fe^{III} , Cu^{I} , Cu^{II} , Co^{II} , Co^{III} , Mn^{II} , Mn^{III} , Mn^{IV} , and MnO_2 .
27. The apparatus of claim 26, wherein said catalyst is MnO_2 .
28. The apparatus of claim 20, wherein said light-activated photolytic catalyst converts water into active oxygen.
29. The apparatus of claim 26, wherein said disproportionation catalyst converts active oxygen to dissolved oxygen.
30. The apparatus of claim 26, wherein said cell is constructed from mesoporous materials.
31. The apparatus of claim 26, wherein said cell is constructed of SAMMS.
32. The apparatus of claim 19, wherein the anode compartment and the cathode compartment are separated by a cationic membrane.

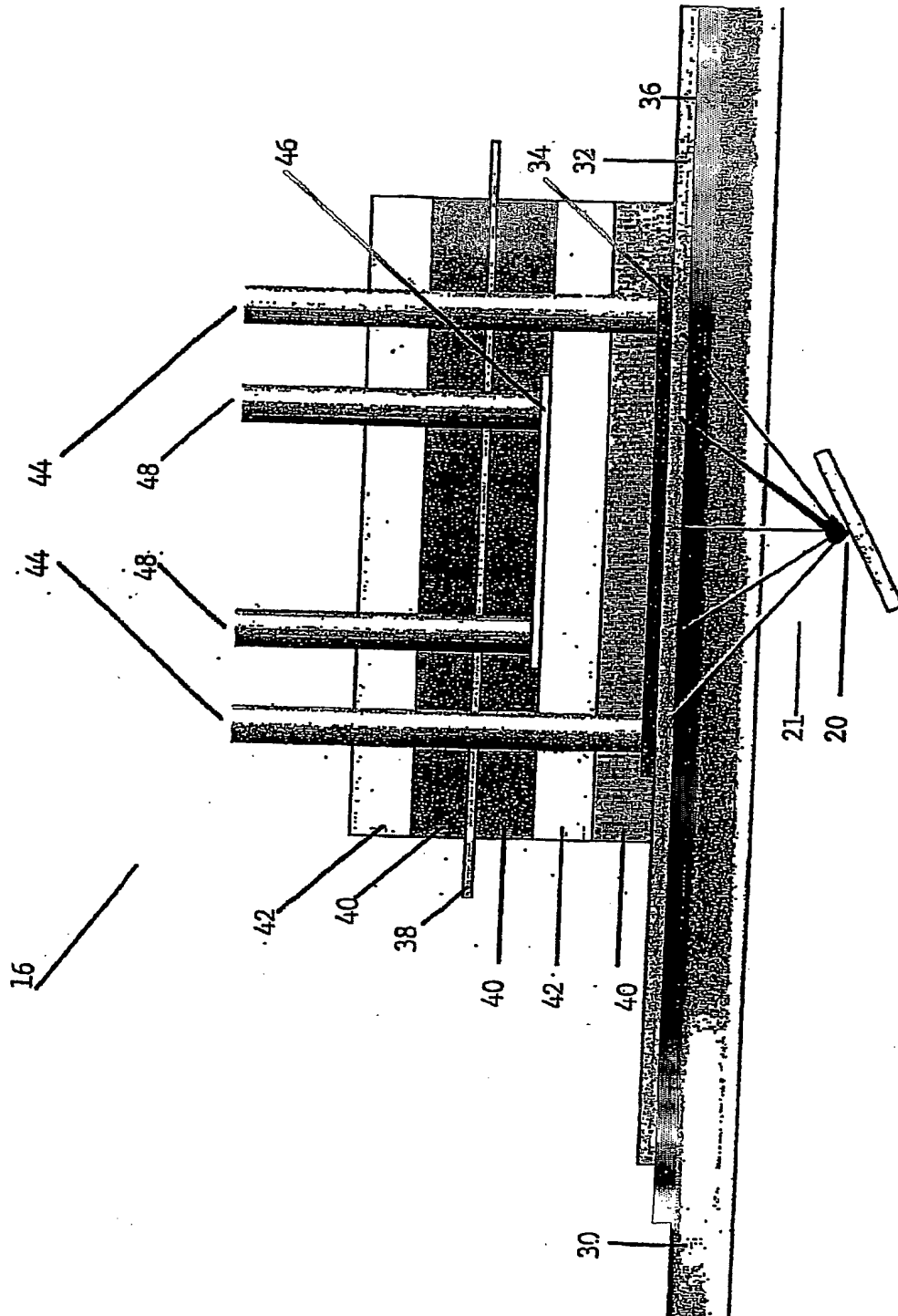


Fig. 1

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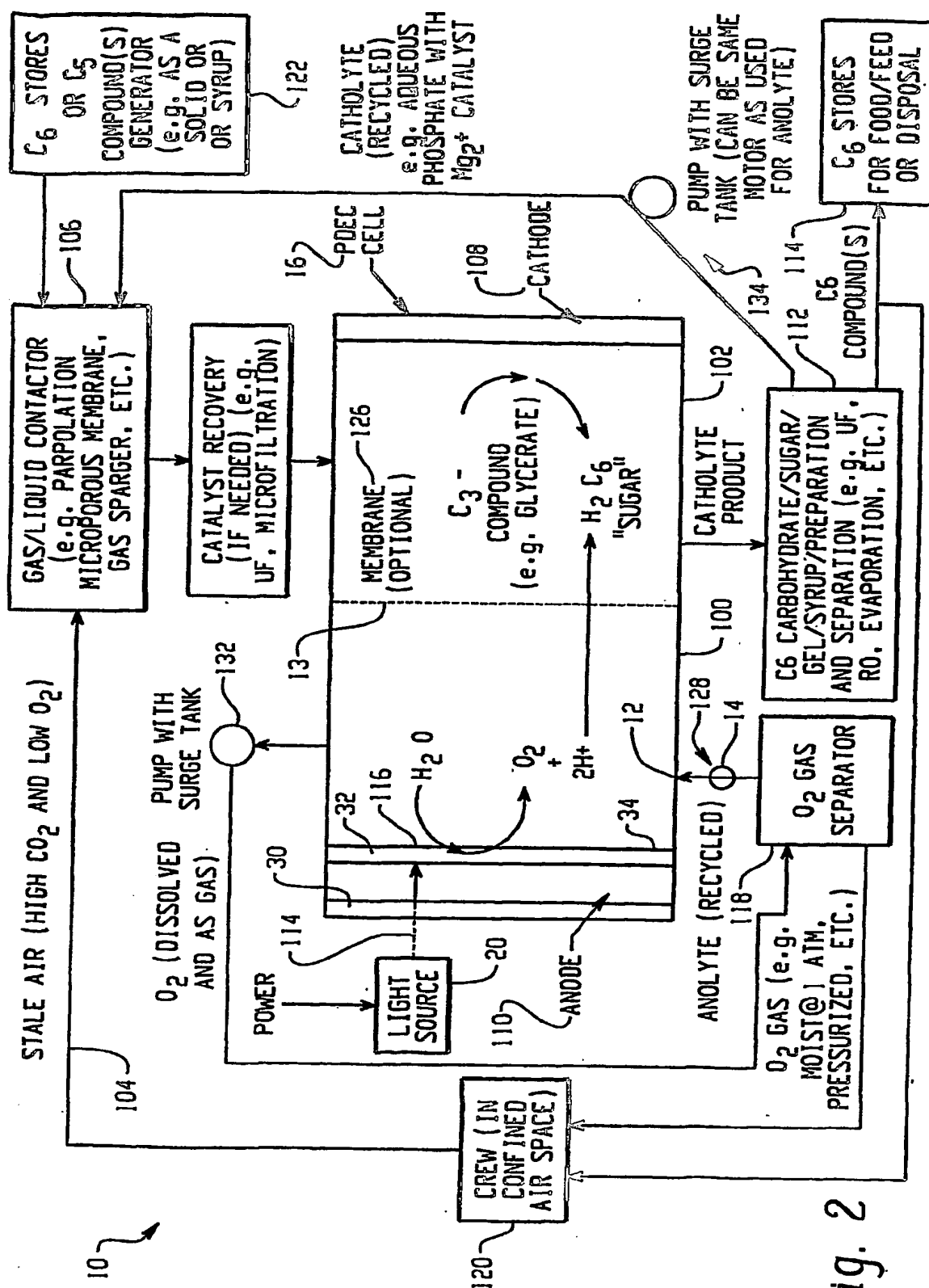
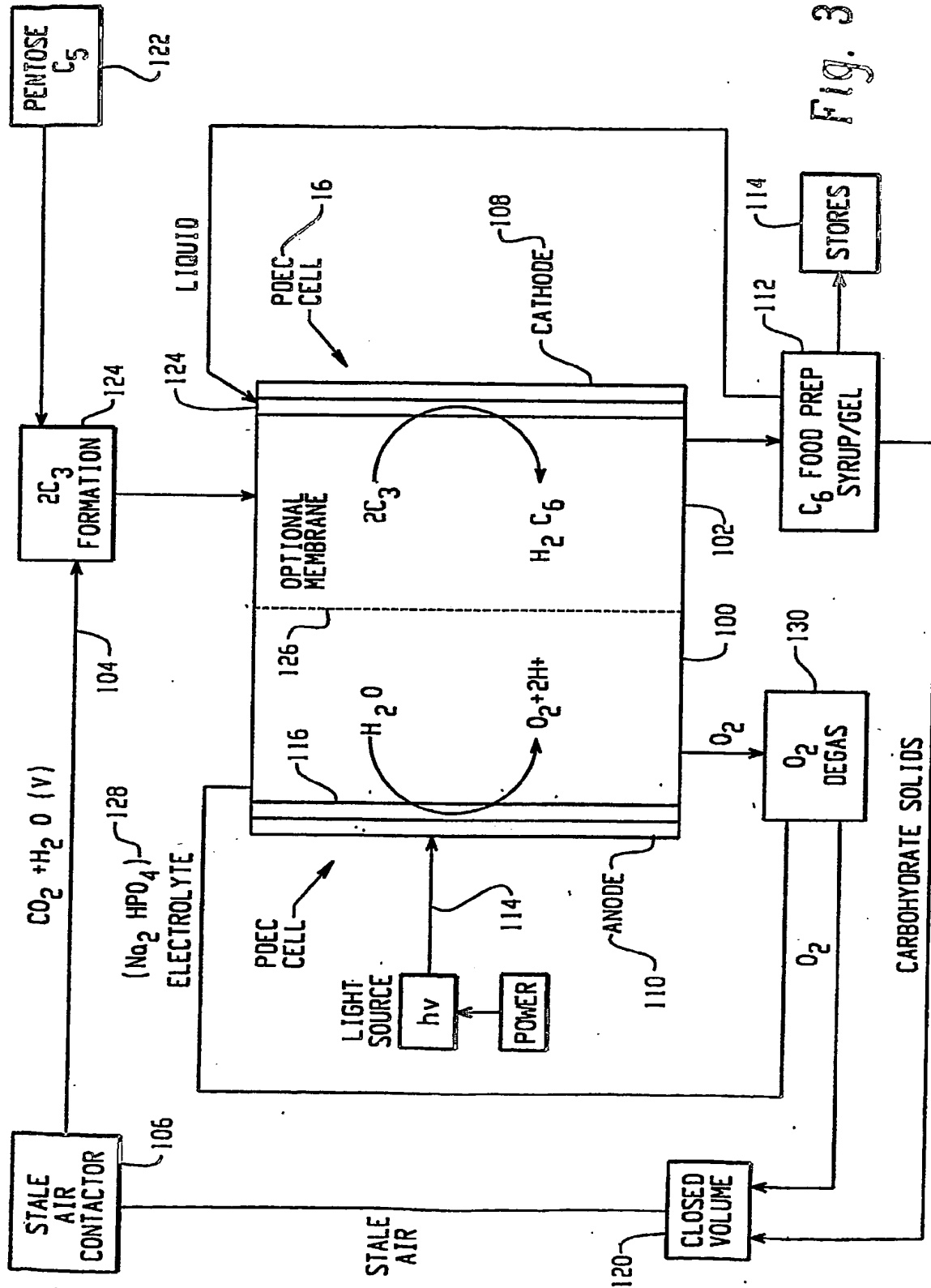


Fig. 2



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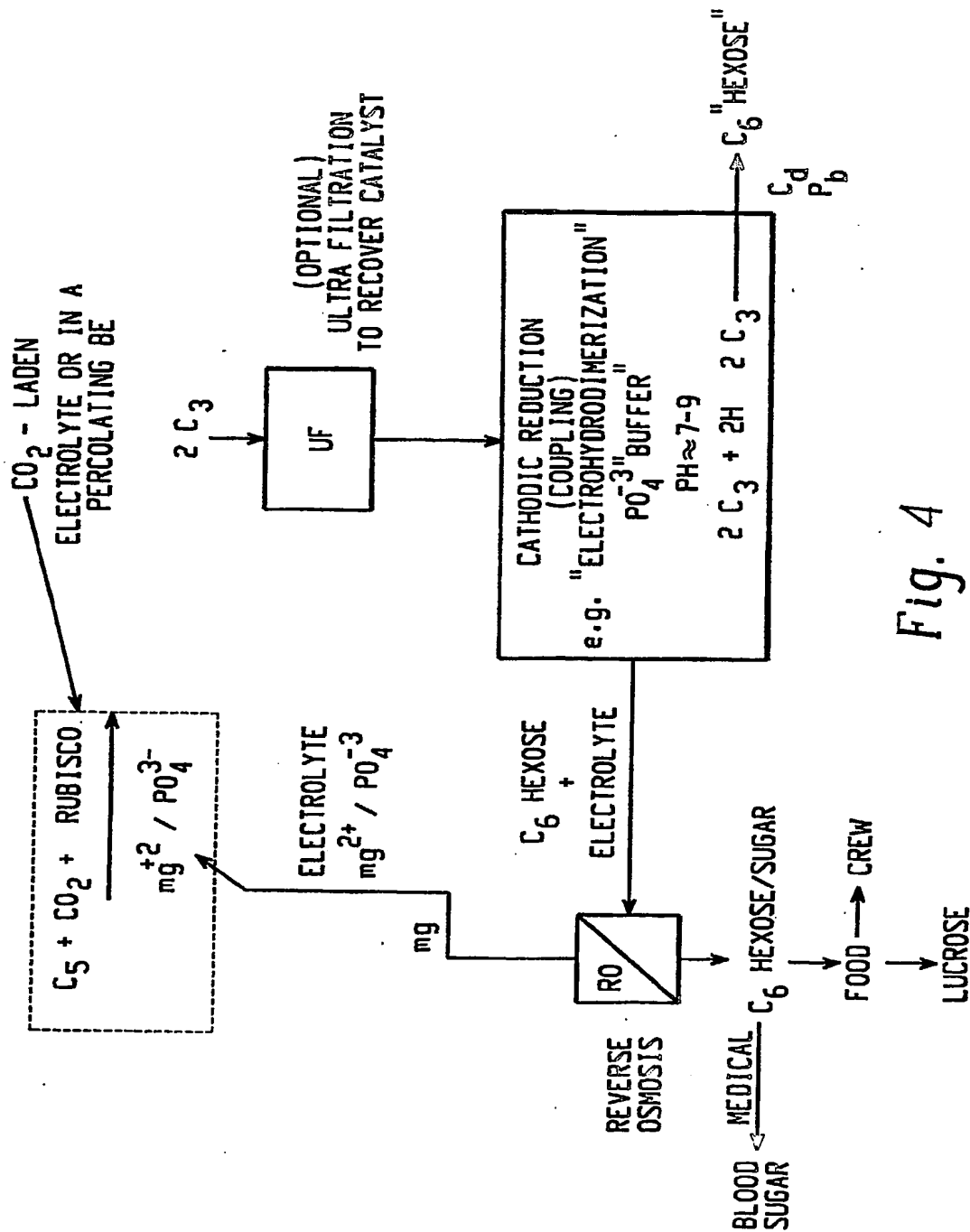


Fig. 4

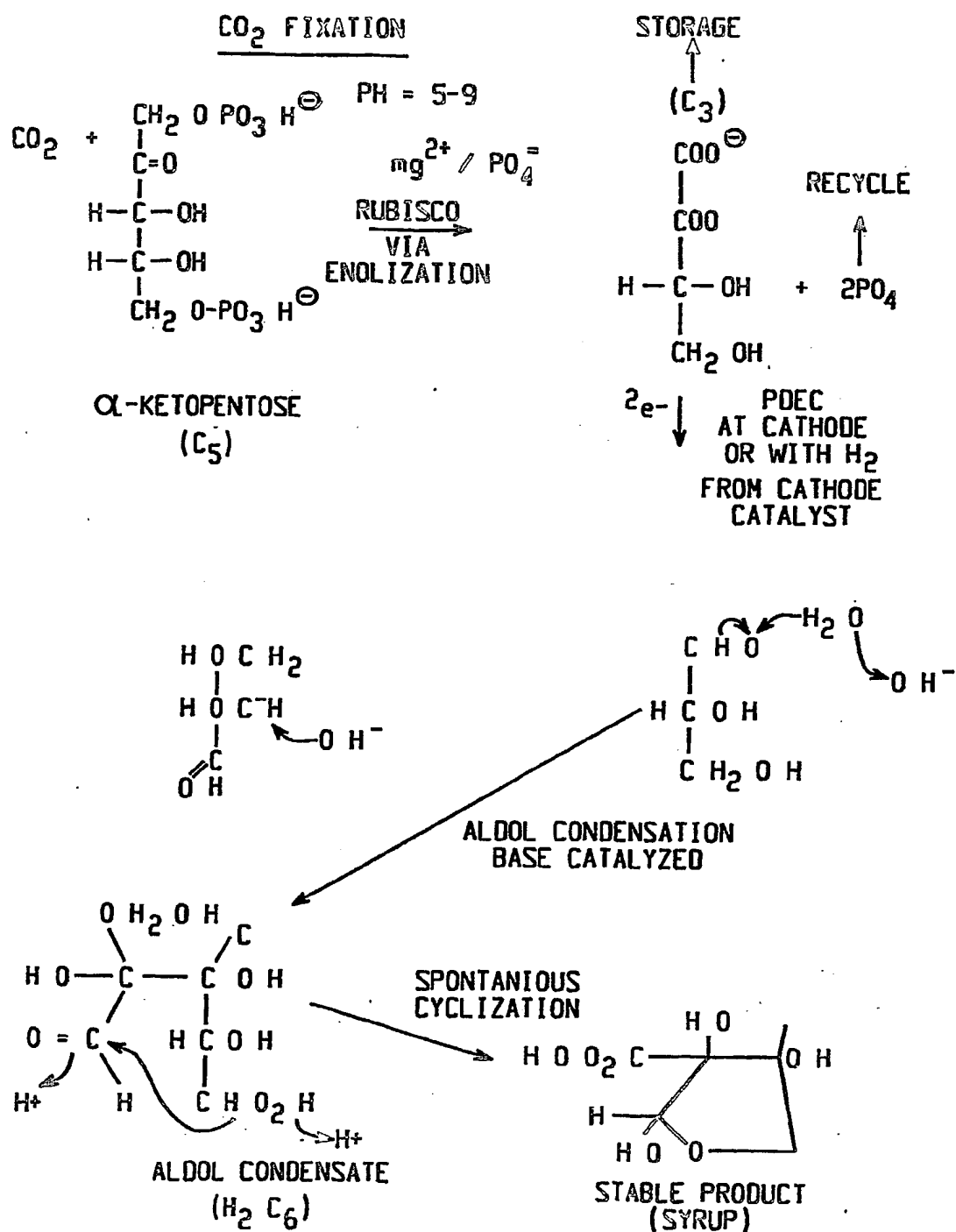


Fig. 5

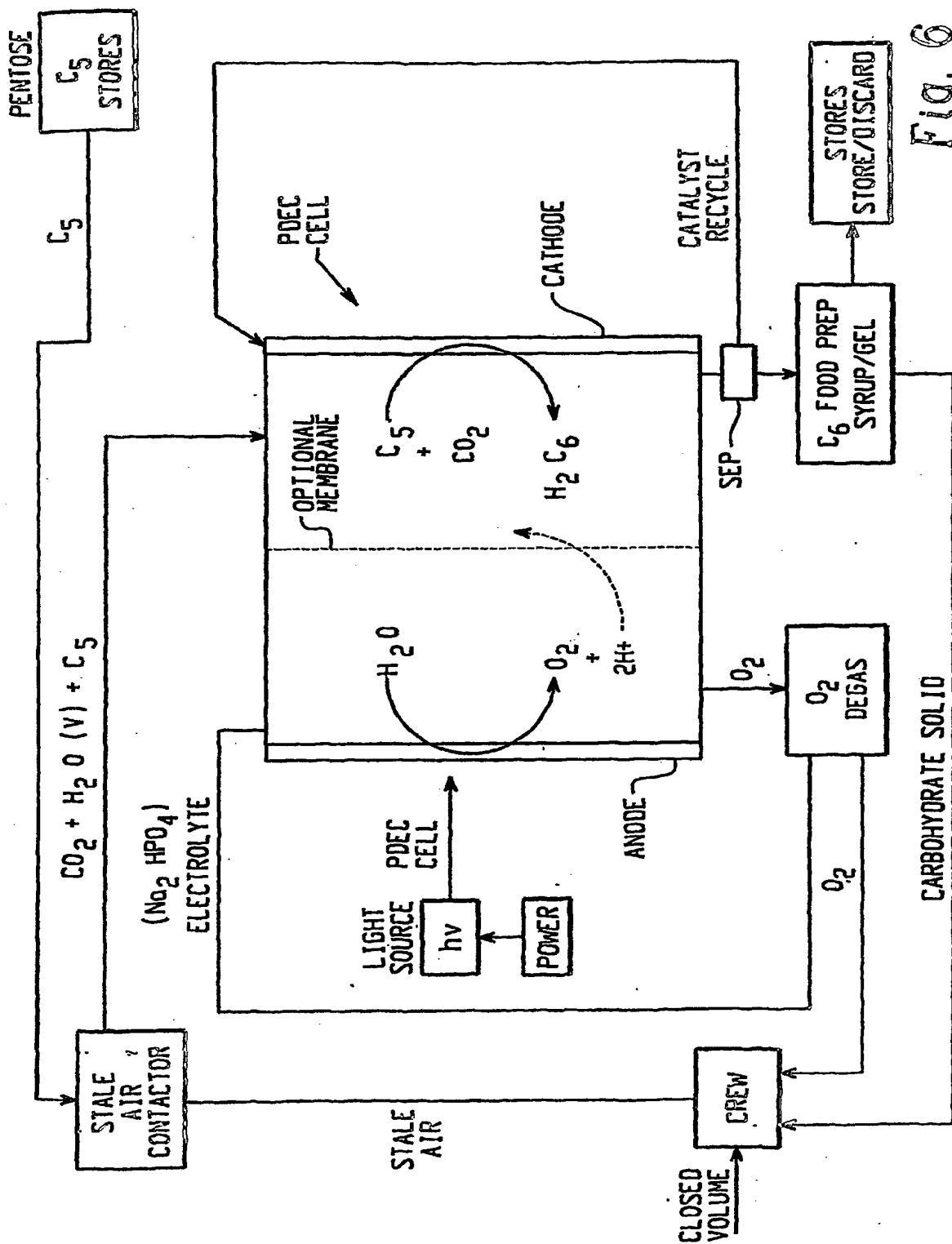


Fig. 6

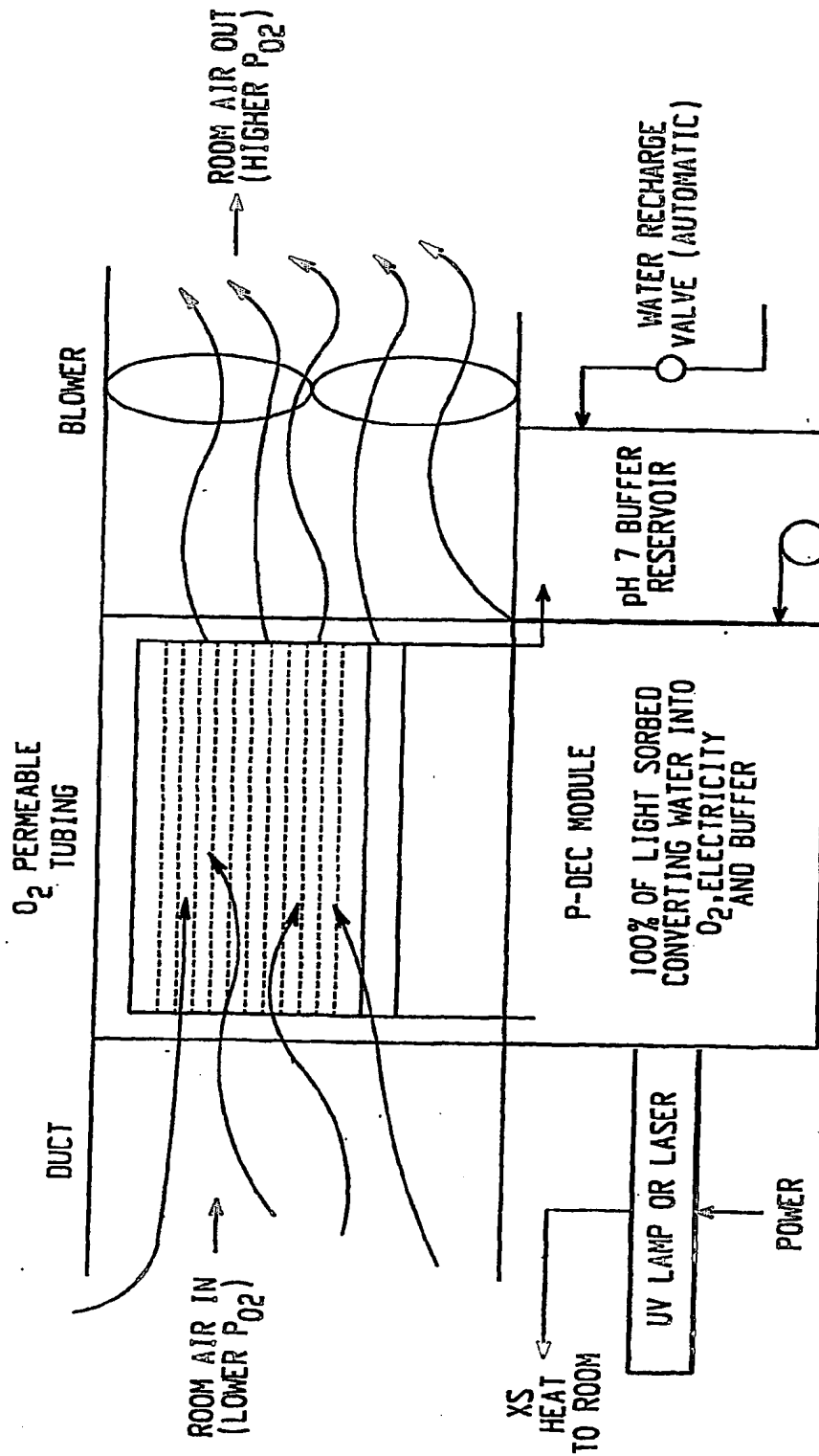


Fig. 7

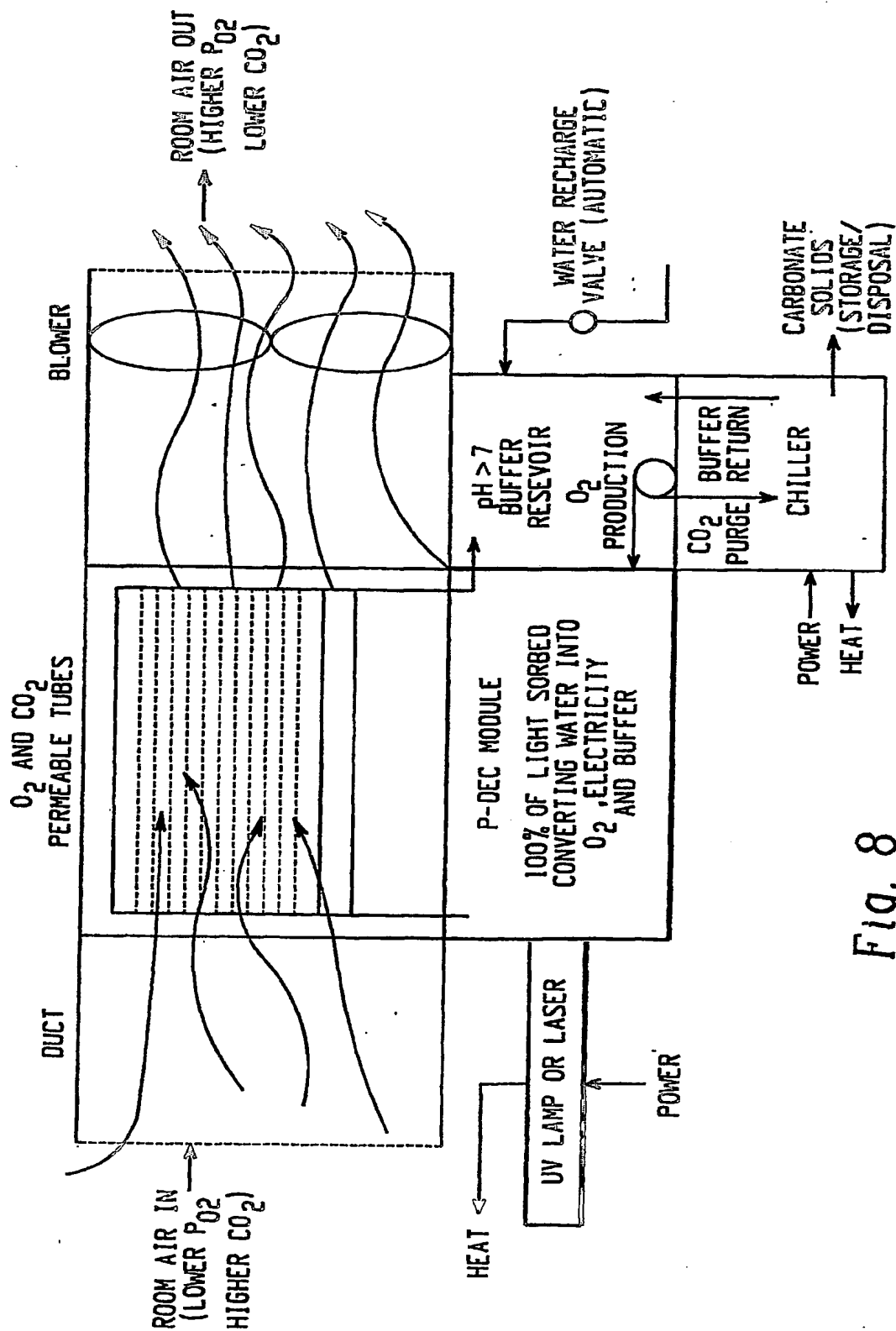


Fig. 8

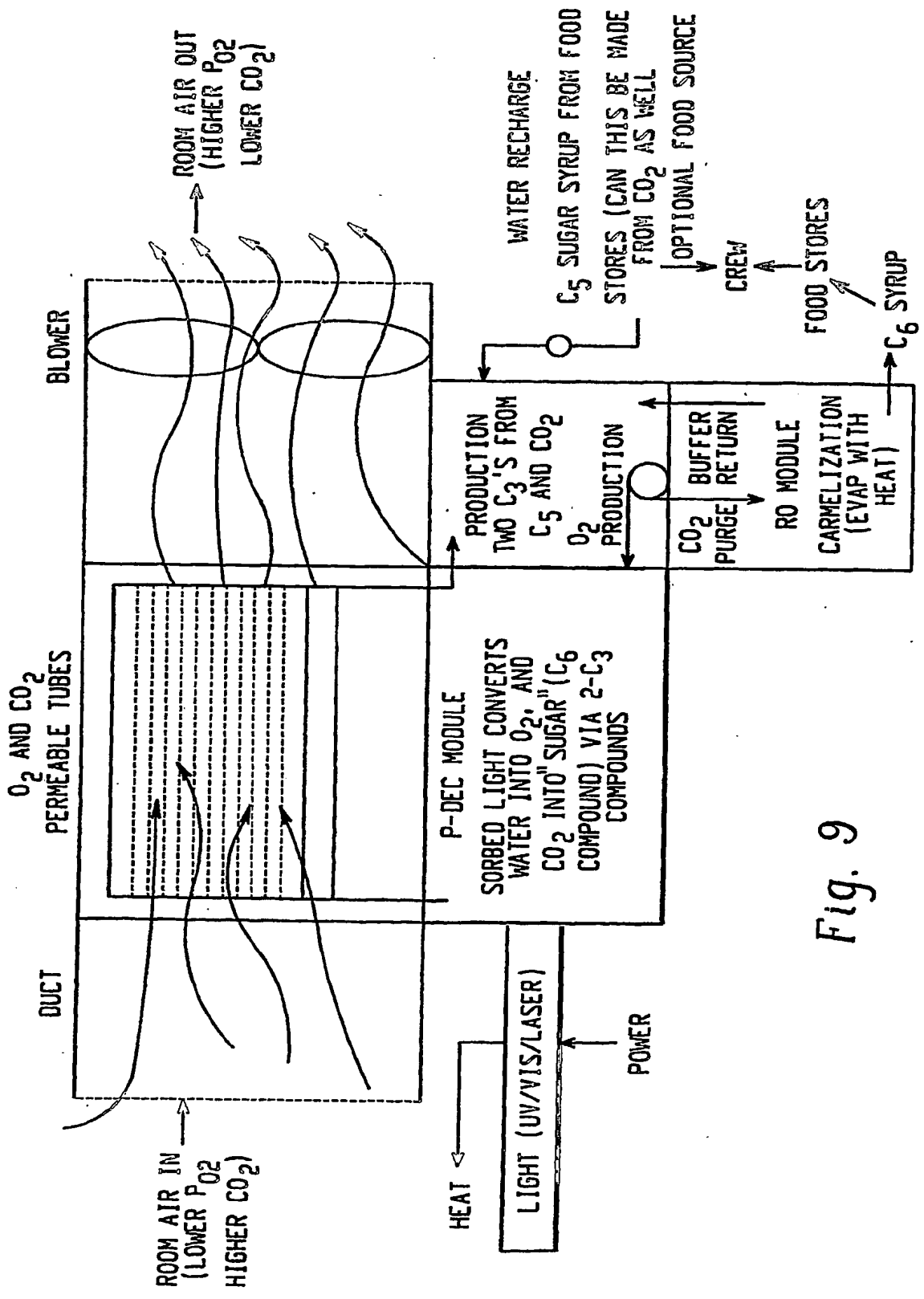


Fig. 9

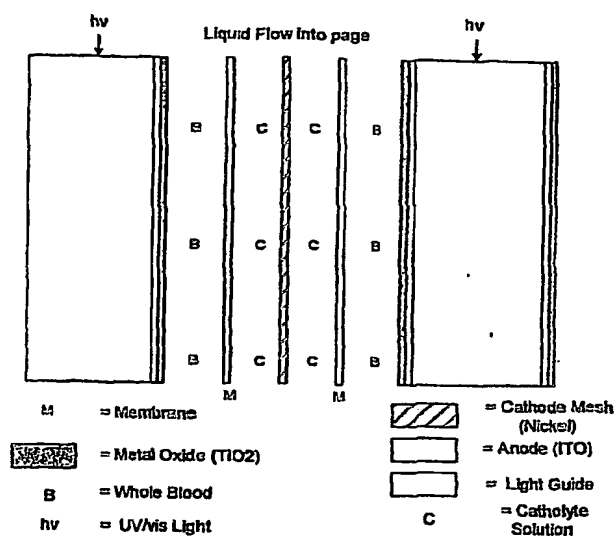


FIGURE 10A

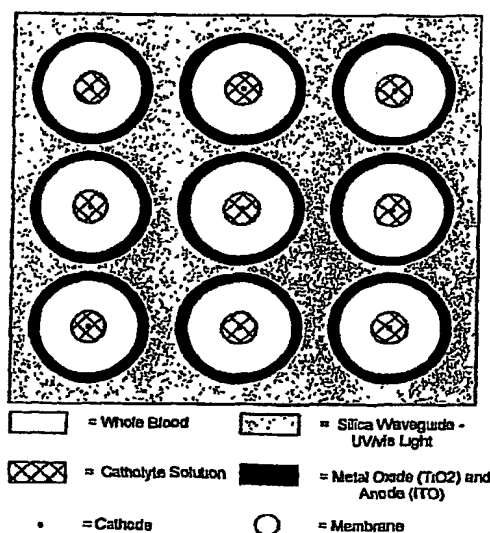


FIGURE 10B

Figures 10A - 10B: Possible geometries for the capillary mimicking structures



FIGURE 11A

FIGURE 11B

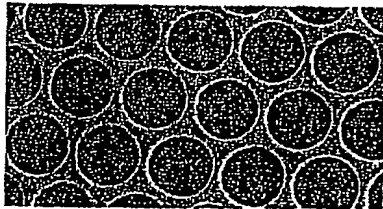
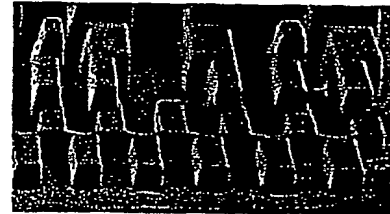


FIGURE 11C

Figures 11A - 11C: Examples of nanopatterned surfaces. Shown are three structures that were generated by photolithography with anisotropic etching in silicon. Left (Figure 11A), light traps. Above right (Figure 11B), ink jet channels. Below right (Figure 11C), EMI mesh filters.

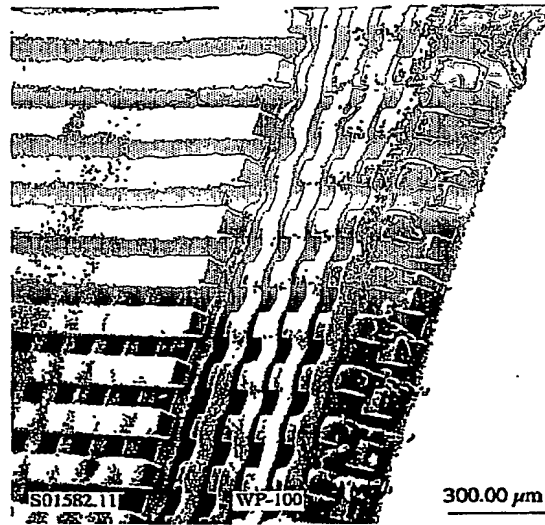


Figure 12: A 3-D mesh structure composed of 100 μ m "sticks" with 100 μ m spacing created by the microfabrication technique developed by Applicant.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US03/26012

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : C25B 1/00; C25C 1/02; C25D 17/00

US CL : 204/242, 252, 263-266; 205/340, 628, 633, 637

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 204/242, 252, 263-266; 205/340, 628, 633, 637

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EAST: photo? same cell; light near3 activated; 204/\$.ccls. and photo? and carbon near3 dioxide

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 4,466,869 A (AYERS) 21 August 1984 (21.08.1984, Figures 1, and columns 4-8.	1-3, 5, 13-14
A	US 4,478,699 A (HALMANN et al) 23 October 1984 (21.10.1984)	

☐ Further documents are listed in the continuation of Box C.

☐ See patent family annex.

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15 June 2004 (15.06.2004)

Date of mailing of the international search report

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